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IRON AND STEEL DIVISION

1934

A. I. M. E.

TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Vol. 113

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Notice

This volume is the seventh of a series containing papers and discussions presented before the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers since its organization in 1928; one volume each year, as follows:

1928, Iron and Steel Technology in 1928
1929, 1930, 1931, 1932, 1933 and 1934, TRANSACTIONS of
the American Institute of Mining and Metallurgical
Engineers, Iron and Steel Division

This volume contains papers and discussions presented at the meetings at Detroit, Oct. 4-5, 1933 and at New York, Feb. 19-22, 1934.

Papers on iron and steel subjects published by the Institute prior to 1928 are to be found in many volumes of the TRANSACTIONS of the Institute; during the past 25 years in Vols. 37 to 45, inclusive; 47, 50 and 51, 53, 56, 58, 62, 67 to 71, inclusive; 73 and 75. Vol. 67 was devoted exclusively to iron and steel.

Iron and steel papers published in the TRANSACTIONS may be found by consulting the general indexes to Vols. 1 to 35 (1871-1904), Vols. 36 to 55 (1905-1916), and Vols. 56 to 72 (1917-1925), and the indexes in succeeding volumes.

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FOREWORD

THE Iron and Steel Division Volume this year contains papers and publications presented at the Fall Meeting at Detroit, Mich., in October, 1933, and at the Annual Meeting of the Institute in New York in February, 1934. Those papers have been selected which, in the opinion of the Papers and Publications Committee, merit a permanent place in the Institute TRANSACTIONS.

The officers and Executive Committee of the Division wish to express their thanks to those who have presented the papers and discussions published in this volume.

Dr. F. N. Speller's Howe Memorial Lecture in February, 1934, "The Corrosion Problem with Respect to Iron and Steel," is worthy of special attention. B. F. Harlan, whose paper on "The Modern Trends in Blast Furnace Operation and Design" was read at the Annual Dinner of the Division in New York, May, 1934, was the winner of the J. E. Johnson, Jr., Award for 1934.

An earnest attempt has been made recently to secure more papers dealing with the practical phases of the Iron and Steel Division's work. The Open Hearth Committee of the Division continues to hold the interest and attention of open-hearth operators and metallurgists. The papers and discussions presented at their meetings each year are published in a separate volume by that Committee. No attempt has been made by this group to sponsor highly technical or scientific investigations. The Division, through this Committee, encourages operating men to discuss their practical problems at these conferences.

In order to increase the efficiency of the various technical committees of the Division, the officers and the Executive Committee propose to add the names of a number of the younger members of the Division to the present committee membership. We believe we should capitalize on the enthusiasm and fresh viewpoint of youth, as well as train them for future leadership in the Institute.

It is the responsibility of each member of the Division to secure the active participation of younger technical and operating men as members of our Division. No organization can rest on its glorious history or its present laurels. We must look to the future. It belongs to youth. We must interest the young men in our work. With the history of accomplishment and the glamour of names of great scientists, past and present, as our heritage, this should not be a difficult task. It means only that each member must make a real effort to do something for his Division and the Institute of which it is a part.

Mr. Howard Eavenson, as President of the Institute for 1934, has said: "By securing a new member we can, in this way, give valuable support to the organization whose primary aim has always been to promote the interests of the industry on which we depend for our livelihood."

The Division conducted a very instructive and important Symposium on Slag Control in the Open-hearth Furnace at the 1934 Fall Meeting in New York.

During the year 1933, Dr. T. D. Yensen and Dr. C. H. Herty, Jr., were appointed to serve as a committee for the Iron and Steel Division to study the simplification and clarification of the nomenclature of Non-metallic Elements in Metals. A number of discussions were held with others who were interested, and criticism of conclusions was asked for and received from a number of well-known scientists and metallurgists in the United States and Europe. The findings of the committee were presented at a joint session of the Iron and Steel and Institute of Metals Divisions at the Annual Meeting in February, 1934. Since then, their report has been published by the Institute under the title of "Terminology Relating to Nonmetallic Elements in Metals" [A.I.M.E. *Tech. Pub.* 555 in METALS TECHNOLOGY for June, 1934] and has been sent to other interested scientific and engineering societies for criticism and possible adoption. The committee will continue its work.

The aim of the Iron and Steel Division is to present papers of interest and benefit to its members. The officers and Executive Committee welcome criticisms of its programs and the type of papers presented at its meetings. It will be helpful if members will suggest the subjects of papers they would like to have presented.

L. F. REINARTZ, *Chairman*,
Iron and Steel Division.

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The Howe Memorial Lecture

THE Howe Memorial Lecture was authorized in April, 1923, in memory of Henry Marion Howe, as an annual address to be delivered by invitation under the auspices of the Institute by an individual of recognized and outstanding attainment in the science and practice of iron and steel metallurgy or metallography, chosen by the Board of Directors upon recommendation of the Iron and Steel Division.

So far, only American metallurgists have been invited to deliver the Howe lecture. It is believed that this lecture would gain in importance and significance were it possible to include metallurgists from other countries, but the Institute has not yet been able to do this on account of lack of special funds to support this lectureship.

The titles of the lectures and the lecturers are as follows:

- 1924 What is Steel? By Albert Sauveur.
- 1925 Austenite and Austenitic Steels. By John A. Mathews.
- 1926 Twenty-five Years of Metallography. By William Campbell.
- 1927 Alloy Steels. By Bradley Stoughton.
- 1928 Significance of the Simple Steel Analysis. By Henry D. Hibbard.
- 1929 Studies of Hadfield's Manganese Steel with the High-power Microscope.
By John Howe Hall.
- 1930 The Future of the American Iron and Steel Industry. By Zay Jeffries.
- 1931 On the Art of Metallography. By Francis F. Lucas.
- 1932 On the Rates of Reactions in Solid Steel. By Edgar C. Bain.
- 1933 Steelmaking Processes. By George B. Waterhouse.
- 1934 The Corrosion Problem with Respect to Iron and Steel. By Frank. N. Speller.

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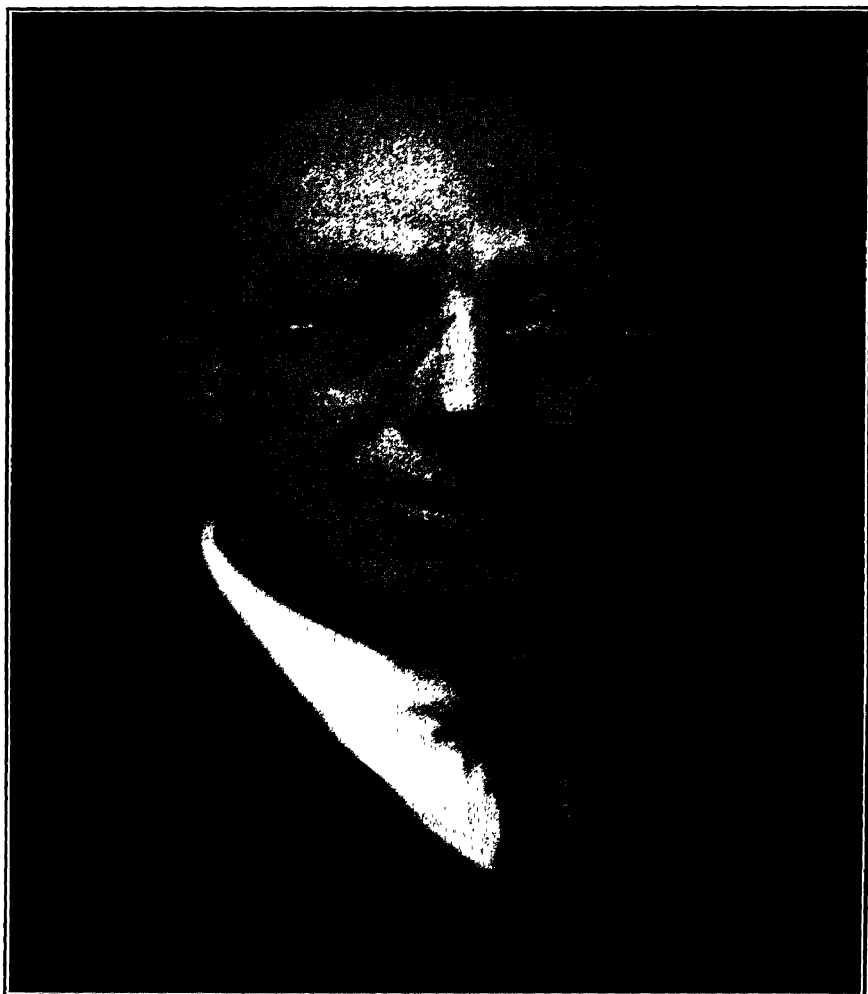
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FRANK. N. SPELLER
Henry Marion Howe Memorial Lecturer, 1934

The Corrosion Problem with Respect to Iron and Steel

BY FRANK. N. SPELLER,* PITTSBURGH, PA.

(Henry Marion Howe Memorial Lecture†)

WE are here to honor again the memory of Henry Marion Howe, one of the foremost metallurgists of his time, and it is indeed a great privilege to be called upon by the Board of Directors of this Institute to give the memorial address this year.

Professor Howe started active investigation of corrosion of iron from a metallurgical standpoint in 1887, and made several important contributions to the subject from 1895 to 1908.^{(1)‡} The papers named in the bibliography are only a few of his valuable papers, but in all his works he sets a high standard of scientific accuracy, together with a clearness and power of expression rarely equaled in engineering literature. Therefore it seems appropriate on this occasion to review the work on corrosion of this distinguished gentleman and then endeavor to make a brief inventory of what has been accomplished since his time.

Howe saw the beginning of the steel industry in America and before he died (May 14, 1922) witnessed it develop to a production of 45,000,000 tons per year. He was naturally very much interested in the infant industry and was quick to see the importance of the question of corrosion.

It was my privilege to discuss the subject of corrosion frequently with Professor Howe at various times from 1905 to 1908; in this, as in other metallurgical problems, he sought the truth without bias and always insisted on proving an opinion or conclusion before accepting it. We should remember that when Howe started his investigation of corrosion, in 1887, steel was rapidly supplanting wrought iron. Certain papers in the early eighties (now forgotten) claiming much greater durability for wrought iron than for steel aroused Howe's interest. He could not reconcile the statement that steel was intrinsically and incurably less durable than wrought iron with the continued and widening use of steel, and went to great pains to analyze the unfavorable experience often cited at that time against steel. After thorough investigation of all the data and opinions produced he was able to show that the evidence in these

* Director Department of Metallurgy and Research, National Tube Co. (Subsidiary of U. S. Steel Corporation).

† Presented at the New York Meeting, February, 1934. Eleventh Annual Lecture.

‡ Superior figures in parentheses refer to the bibliography at the end of the paper.

papers was untrustworthy and there were probably no grounds for the prevailing opinion that steel was inherently and generally inferior to wrought iron in durability. He recognized the need for more extensive study of this problem and in 1897 started comparative tests in fresh water, sea water, and in the atmosphere, on a scale nearly twenty-five times larger than any former test. He summarized all the work previously done on this subject, in important papers before the International Society for Testing Materials in 1900 and before the American Society for Testing Materials in 1906 and 1908.⁽¹⁾ His general conclusion was that the data then available showed no material difference between wrought iron and steel in loss of weight under most conditions. The influence of environment on both the actual and relative rates of corrosion was apparent, and yet Howe had a strong feeling that the instances cited of exceptionally short life of steel might be due to exceptionally poor material. Furthermore, the unusual life occasionally reported for wrought iron was probably due to favorable environment and was not typical. This has been amply substantiated by later experience. Since better control over the uniformity of steel has been obtained, this factor has been shown to be less significant than other factors that are entirely independent of the metal. He pointed out later that the depth of pitting should be determined, as well as loss in weight; that the tests should be continued to destruction, and that all previous tests (including his own) were incomplete in this respect. He summed up the situation briefly and clearly in 1906 in the following words:^(1c)

On one hand we have the very general public opinion that steel corrodes not only faster but very much faster than wrought iron, an opinion held so widely and so strongly that it cannot be ignored. Smoke does not prove that fire exists; but such a strong smoke bids us look carefully for fire. On the other hand, we have the results of direct experiments by a great many observers, in different countries and under widely differing conditions; and these results certainly tend to show that this popular belief is completely wrong, and that on the whole there is no very great difference between the corrosion of steel and wrought iron.

Admitting that the experimental data were not altogether trustworthy, he pointed out that much of the so-called practical experience cited in this controversy was even more questionable, and that, as several influences were working together, exceptionally short life might be expected with either material under certain conditions. He refused to be stampeded by opinions or untrustworthy data and demanded real evidence on a sufficient scale before drawing final conclusions. Howe's summary of this subject in the early part of this century probably prevented hasty conclusions detrimental to steel and paved the way for the more complete experimental work that followed. He did not attempt to discuss the theories of corrosion, on which subject there was much con-

troversy at that time, but concentrated his investigation on the questions that seemed to be of more immediate importance to manufacturer and consumer.

The first steel pipe was made in 1886. The opposition to the substitution of bessemer steel for wrought-iron pipe was strong and often bitter. Plumbers were quoted as reporting that they found wrought-iron pipe, more durable than steel and that they could easily distinguish one from the other in threading. The opinion of the so-called practical man was listened to with respect. Pipe was not marked in those days and frequently became mixed in the stocks. Howe investigated the reliability of plumbers' opinions on this matter by sending mixed lots of pipe (half iron and half steel) to four reputable operators, asking them to thread all of the samples and report how many were wrought iron and how many were steel. The results were so far from the facts that, as Howe pointed out, they would have come just as near the truth by tossing a coin.^(1c)

The controversy on wrought iron vs. steel has been reviewed at some length, not because the subject is of any great importance at present, but because of the part that Professor Howe took in the debate that waged on this subject for a generation or more. As a matter of fact, the proportion of wrought-iron production with respect to steel has apparently become more or less stable, for during the past 10 years in the United States the annual production of rolled iron ranged from 1 to 3 per cent of the rolled iron and steel, while in the same period wrought-iron pipe ranged from 4 to 5 per cent of the wrought pipe.

These figures, of course, do not indicate the situation as it might have been influenced by an earlier development of the Aston process for the production of wrought iron. The recent introduction of this process for making cinder-bearing wrought iron from bessemer steel is probably the most notable economic development in the wrought-iron industry since puddling came into use.

CORROSION PROBLEM TODAY

Let us now briefly review the corrosion problem as we find it 25 years later. On account of the limited time at my disposal this afternoon it is necessary to select for discussion only the more important developments and avoid going into much detail, but the reader is referred to more recent publications for further information on various phases of the subject. Since Professor Howe's last report on relative corrosion in 1908, many long-time tests to destruction have been completed. Table 1 gives a brief summary of Howe's tests and several other typical tests more recently completed on the same kind of material. The relative standing of these materials, based on maximum depth of penetration, is practically the same under most conditions as that found by Howe and other early

TABLE 1.—*Summary of Average Results of Relative Corrosion Test Made by Howe in 1900, also Some More Recent Tests*

Authority and Date of Test	Material and Time Exposed	Atmosphere	Fresh Water	Sea Water	Soil
Howe (1900).....	Bessemer steel—2 years ^{a,d} Wrought iron—2 years ^{a,d}	100.0 97.3	100.0 106.7	100.0 83.9	
A.S.T.M. (1916-1932).....		Pittsburgh 22 ga. (6.25 yr.)	Washington 16 ga. (7.4 yr.)	Key West Portsmouth 22 ga. (5.45 yr.) (4.26 yr.)	
	Bessemer steel ^{b,d} Wrought iron ^{b,d}	100.0 60.4	100.0 103.1	100.0 121.2	100.0 114.9
	Copper bessemer steel ^{b,d}	less than } 22.9 ^d less than }	less than } 54.2 ^d less than }	83.5 98.4	
Pipe Service Tests sponsored by National Tube Co. (1910-1931).....	Bessemer steel, 1 to 12 years ^{b,e} Wrought iron, 1 to 12 years ^{b,e} Copper steel, 1 to 12 years ^{b,e}	100 92 35	100 115 90	100 138	
Friend's Tests, England (1922-1932).....		Birmingham Gas Works (3 yr.)	Birmingham Technical College (7 yr.)	Bristol Channel (4 yr.)	
	Steel ^{a,f} Wrought iron ^{a,f} Copper steel ^{a,f}	100.0 68.5 55.5	100.0 103.4 101.1	100.0 77.9 75.8	
U. S. Bureau of Standards (1922-1932).....	(a) Bessemer steel, 10 years ^{a,e} Wrought iron, 10 years ^{a,e} (b) Bessemer steel, 10 years ^{a,e} Wrought iron, 10 years ^{a,e}				100.0 100.7 100.0 97.8

^a Measured by loss in weight.^b Measured by depth of pitting.^c Thirty-six ¼-in. plates (24 by 16 in.) of each material were exposed to sea water at Sandy Hook, to fresh water in the Haritan River at High Bridge, N. J., and to the atmosphere at High Bridge, N. J.^d In the atmospheric test approximately 225 sheets (30 by 96 in.) were exposed at each location. In the immersion test 150 sheets (6 by 2 in.) were exposed at each location. At the end of the atmospheric test, 18 out of 23 copper bessemer steel sheets had not failed at Pittsburgh, and 23 out of 23 had not failed at Ft. Sheridan.^e Averages of 35 tests in hot fresh-water pipe lines, 9 in atmospheric vent pipes and 1 in hot salt water.^f The fresh-water test was a laboratory test in tap water in which the specimens were 1-in. bars, 3 in. long. The atmospheric and sea-water tests were field tests in which 1-in. bars 2 ft. long were used.^g A cooperative test conducted by the Bureau of Standards in 47 soils throughout the United States. The figures given are averages of 6 steel and 4 wrought-iron pipe specimens in each of 22 of the more corrosive soils.

investigators, based on loss in weight. Steel made during the past 25 years is undoubtedly more uniform, and this may explain why steel now apparently compares so favorably with wrought iron with respect to the tendency to pit. However, it now seems probable that the general opinion that prevailed a generation ago in favor of wrought iron was based mostly upon visual observations made under atmospheric conditions, rather than on less accessible material in soil or water where the composition of the metal has been shown to be a much less important factor. Moreover, the older wrought iron, made mostly from eastern ores, usually carried higher copper content than steel of that period, which we now know improves its resistance to atmospheric corrosion.

While much has been done to mitigate corrosion, it is still recognized as a world-wide problem similar to public health in general interest. About 1200 million tons of iron and steel products were in use in 1931, according to Sir Robert Hadfield.* The total amount of steel ingots and castings produced in the world to date is about 2400 million tons which represents about 1700 million (long) tons of finished product. In recent years the steel produced amounts to about 18 times the total tonnage of all nonferrous metals. The world production of the more commonly used metals for the past 11 years, in short tons, is given in Table 2.

TABLE 2.—*World Production of Metals^a*

Year	Steel	Copper	Aluminum	Zinc	Lead
1923	86,355,360	1,411,980	153,288	1,059,821	1,314,001
1924	86,832,480	1,522,394	184,475	1,125,188	1,467,265
1925	99,906,240	1,589,717	197,919	1,265,714	1,669,854
1926	102,925,760	1,637,489	215,331	1,373,212	1,770,278
1927	112,981,120	1,682,361	242,256	1,464,091	1,857,998
1928	120,374,240	1,892,350	281,893	1,566,919	1,841,012
1929	132,137,600	2,127,834	310,762	1,620,898	1,932,520
1930	104,223,840	1,733,706	295,397	1,557,644	1,848,070
1931	76,293,280	1,481,969	240,327	1,113,172	1,535,457
1932	55,816,320	972,720	171,898	875,135	1,285,728
1933	73,114,720	1,082,000	150,750 ^b	1,007,000	1,320,000

^a From *Metal Statistics*.

^b Estimated.

These figures illustrate the indispensable position that steel products occupy in the world at present, in spite of their relative susceptibility to deterioration under some conditions of service.

About three-fourths of the iron and steel products require some kind of protection if only for the sake of appearance. Sheets, plates, wire, and pipe often have a comparatively short life without adequate protec-

tion. Idle metal, unfortunately, corrodes at a faster rate than busy metal. This fact has been well demonstrated in the past three years in the case of idle mills, smoke stacks, ships, cars, and similar steel construction. The hulls of ore carriers on the Great Lakes are usually not repainted after launching and up to the period of the depression showed very little deterioration. After two years lay-up in the harbors many of these hulls were pitted over $\frac{1}{8}$ in. deep. The rate of corrosion of unprotected iron or steel varies with the environment from an insignificant amount to $\frac{1}{2}$ in. penetration per year. Assuming that the average useful life of iron and steel products is 50 years and that 700 million tons are now in use in the United States, the amount produced last year in this country would have been hardly sufficient for renewals made necessary by corrosion. Hadfield estimated the world's wastage of iron and steel in 1932 to be 67,000,000 tons, which would indicate a loss in the United States nearly three times as large as my estimate. To this must be added the expense of renewal, interruption to business, and other incidental expenses, which as a rule considerably exceed the cost of the metal. However rough these estimates are, they serve to illustrate the importance of the problem to the iron and steel industry and to the taxpayers at large.

Corrosion of iron and steel is now recognized to be not a single problem but a group of problems complicated by many variables, the resultant of which determines the rate of attack. Any review of corrosion data and remedial measures that have been worked out in recent years would be incomplete without a word on the fundamentals of the problem. At the time of Howe's last paper on this subject in 1908, investigations were being planned, or were under way, on the influence of oxygen concentration, temperature, rate of motion, film protection, and many other factors. When more facts became known about these phenomena, it was found convenient to classify corrosion according to the environment, so we now speak of it as atmospheric, underwater, soil, or chemical corrosion, or electrolysis due solely to stray electric currents. Certain specific factors have been found to control the rate of attack in each type of corrosion. In atmospheric corrosion, the predominant factor is the moisture; in water, the oxygen concentration; in soil, the electrical conductivity, total acidity, drainage, etc. The principal factors that have been recognized and studied are listed in Table 3 and are grouped for convenience according to whether they are mainly a function of the metal or of the environment.

The environment as a rule influences both the actual and relative rate of corrosion of a metal much more than the ordinary variations found in the metal. It has been demonstrated that all base metals such as iron, copper, aluminum, etc., acquire a film when exposed to air at normal or elevated temperatures, and that it is usually the resistance of this surface film that determines the life of the metal rather than some internal

property, for the metal usually does not come into direct contact with the attacking medium. Metals such as chromium, nickel, copper, and aluminum form very resistant films in some environments but not in others, and such elements have the power of conferring on iron, when alloyed with it in solid solution, some of their film-building power according to the amount of alloying elements present. The determination of the amount of film-forming constituents that will give the maximum corrosion resistance to iron at the lowest cost is a promising but difficult field of research.

TABLE 3.—*Factors with Reference to Corrosion in Presence of Water*

I. FACTORS ASSOCIATED MAINLY WITH THE METAL	II. FACTORS THAT VARY WITH THE ENVIRONMENT
1. Standard single electrode potential	1. Effective potential ^a
2. Composition and chemical homogeneity	2. Concentration and distribution of dissolved oxygen
3. Structural homogeneity; solid solutions, separate aggregates, amount and distribution of nonmetallic inclusions, etc.	3. Hydrogen-ion concentration
4. Surface finish	4. Specific nature and concentration of other ions in solution
5. Inherent power to form surface films	5. Velocity of motion of solution
6. Internal strain	6. Temperature
7. Over-voltage of hydrogen on the metal surface	7. Deposits of corrosion products
	8. Contact with dissimilar materials

^a The potential is dependent upon composition of metal and electrolyte, temperature and other factors listed above. Surface film formation is also a function of both the metal and environment.

Recent study of the surface films on metal has thrown a new light on the mechanism of corrosion. The presence of invisible films has been demonstrated by separating the film from the metal so that the film can be examined under the microscope, and their growth has been traced by their effect in changing the potential of the metal when immersed in a suitable electrolyte. Much more is known about the physical properties and structure of metals than about their surface condition but it is now definitely known that, at least in the case of the common metals, we are dealing with a film-covered surface and not with a real metallic surface.

Protective surface films are formed by reaction between the metal and its environment, usually by oxidation. The essential film-building materials may originate mainly in the metal (as in stainless steels), in the environment (as in passivation with nitric acid or chromates), or both metal and environment may contribute their share in building the film.

The stability of films has been found by Vernon⁽³⁾ and Evans⁽⁴⁾ to vary materially with the conditions of initial exposure. When the environment is very favorable to the formation of a dense adherent film, unusual resistance to corrosion has been obtained even with ordinary wrought iron and steel, which admittedly are vulnerable under normal

conditions. This fact seems to explain the long life occasionally experienced with old wrought iron and steel. Cases have been reported in which, on removal of the initial corrosion products from well preserved iron and steel and exposure of the clean surface to ordinary air, rust developed rapidly. The nature and stability of the metal surface film are now considered to be among the most important factors determining the course of corrosion. Local differences of potential due to concentration cells or contact with dissimilar materials may be sufficient to break down the film even on stainless steel and cause pitting.

In speaking on the phenomena of corrosion in general, there is not enough time to discuss in such detail all the important factors listed in Table 3. Some of these factors, such as local variations in concentration of solution, dissimilar metals in contact, or internal strain, influence the formation of surface films and the distribution of corrosion, while others such as temperature, velocity of flow, acidity or alkalinity, and dissolved oxygen more often determine the rate at which the corrosion process proceeds. In the bibliography at the end of the paper, publications are listed that give detailed information on these and other factors having to do with the mechanism of corrosion reactions, and other phases of the subject.

Complete knowledge of the controlling factors involved is of particular importance in corrosion testing. The influence of any one factor on the rate and distribution of corrosion can be determined only by carefully controlled laboratory tests, but the actual rate of attack should be determined by carefully planned tests in service, as natural corrosion is the result of a changing combination of factors, usually difficult to reproduce in the laboratory. Therefore, while laboratory short-time tests often give a useful indication of the trend and rate of corrosion, the results should not be considered as conclusive unless the laboratory test has been correlated previously with long-time tests in service. For instance, tests of ferrous alloys in sulfuric acid have proved utterly unreliable as an indication of the relative life of these materials in the atmosphere or in water, but on the other hand it has been found that nitric acid, under controlled conditions, gives a fairly satisfactory indication of the relative resistance of high-chromium ferrous alloys under oxidizing conditions.

PREVENTIVE MEASURES

Let us now consider what has been done during the past few years in the reduction of waste due to corrosion. Prevention of this "disease of metals" may be accomplished to a certain degree by: (1) changing the environment; (2) isolating the metal from destructive environment; or (3) building up the corrosion resistance of the metal. All of these methods usually are based upon the principle of forming a protective layer of some kind on the surface of the metal, which may vary from a few molecules to an applied coating $\frac{1}{2}$ in. or more in thickness.

There is no panacea for prevention of corrosion. It is an economic problem and the solution in any specific case requires the best judgment of chemists and engineers working together. In some cases the first result of a thorough study of a corrosion problem has been the discard of wasteful and inefficient means of protection, followed by the development and adoption of more effective and more economical methods. For lack of time we will consider only a few practical applications of the principles of corrosion prevention.

Neutralizers, Passivators, or Removal of Oxygen

Where the corroding medium is limited, it may be made less active by the addition of neutralizers, passivators, or by the removal of free oxygen. Much has been accomplished by such means. In the refining of corrosive crude oil, for instance, ammonia is injected to reduce corrosion due to the generation of hydrochloric acid at temperatures below 400° F. At higher cracking temperatures corrosion by sulfur compounds can be held in check by the use of lime or caustic soda. One of the American Petroleum Institute committees made an extensive report in 1932 on the use of neutralizers, which points out the important factors involved.⁽⁶⁾ This method of controlling corrosion is more generally used in the low-temperature range of refinery operation. It is estimated that in the United States \$3,000,000 per year is spent for neutralizers in the refining of petroleum.

At normal temperatures industrial water can often be treated so that it will be less active and maintain a protective deposit on pipe lines without undue cost or impairing its quality for domestic purposes. It should be remembered that all chemical methods require careful control by qualified industrial chemists. Waterworks engineers have done much to improve the hygienic properties of our water supply and are now giving more attention to the corrosion problem.

The damage to large water mains is not confined to deterioration of the metal but often results in a reduction of 50 per cent or more in the rate of flow due to increase in frictional loss. In the case of heat exchangers the corrosion products have been shown to result in a considerable loss in heat transfer efficiency.⁽⁷⁾ The use of carefully regulated lime-alum treatment in Baltimore has considerably reduced pipe maintenance cost to the city and loss and inconvenience to consumers at an additional cost of only 22¢ per million gallons for lime used to absorb carbon dioxide and maintain the water at a pH of about 8.⁽⁸⁾ Satisfactory results have been reported from Washington, D. C., by use of similar treatment.

Where the water is not used for domestic purposes more drastic treatment may be applied. In condensers or cooling systems where the water is recirculated, the addition of about 100 p.p.m. of sodium chromate in a slightly alkaline water will practically inhibit corrosion at a cost per year

of about \$100 per million gallons of water treated. A much larger amount of inhibitor is required for control of brine corrosion in refrigerating systems but it has been estimated that this treatment, which is now frequently used, is saving the industry a million dollars per year in maintenance charges.

The conditioning of boiler water for the control of scale, wet steam, corrosion and embrittlement is no longer a mystery. Nowhere has greater progress been made in anti-corrosion treatment. With proper design of equipment for mechanical removal of dissolved oxygen and suitable chemical conditioning to maintain a safe alkaline ratio to avoid embrittlement, under the control of a qualified chemist, safe and economical operation can be obtained within the present range of temperatures and pressures.⁽⁹⁾

In district heating there is still some trouble due to oxygen and carbonic acid in the hot condensate lines. This problem is complicated by air leakage in the return lines of vacuum heating systems. However, the power plant engineer should now be able to supply steam sufficiently low in oxygen and carbonic acid so that there will be no material action on steam lines and accessories, provided that air does not find access into the system in some other way.

Isolating Metal from Destructive Environment

The second method of retarding corrosion, by separating the metal from direct contact with the corroding agency, includes all kinds of protective coatings, metallic and nonmetallic, ranging in thickness from ordinary paint to portland cement concrete $\frac{1}{2}$ in. or more in thickness.

An average of 120 million gallons of paint per year has been used in this country during the past 10 years for the protection of iron and steel structures. Some of these paint products have been considerably improved in recent years by the use of synthetic resins, tung oil, and rubber derivatives in the paint vehicle, particularly when used for protection of material exposed to the atmosphere, but most of these materials have not proved so durable when used in water or soil. The development of paints for service under water deserves more attention. Standardized methods of tests for paint films in water should be formulated so that these products can be studied comparatively, as has been done by the American Society for Testing Materials in their atmospheric tests of paints. The results of such work would find an immediate practical use in the better protection of ship hulls, water tanks and similar construction.

Porcelain enamel and chromium plating are finding a wider field of use where galvanized coatings or paints are not sufficiently durable. None of these thin coatings, however, have proved fully adequate so far

for the protection of metal in corrosive soil. The output of vitreous-enameled and chromium-plated steel products has shown a healthy increase during the past few years.

There are now in use in this country about 400,000 miles of pipe lines for the transportation of gas, oil, and water. About 10 per cent of these lines should be carefully protected with strong coatings. The corrosion damage to underground oil and gas pipe in this country has been estimated as high as \$50,000,000 per year.⁽¹⁰⁾ The United States Bureau of Standards has been investigating soil corrosion for 10 years, with the cooperation of the American Petroleum Institute, American Gas Association and pipe manufacturers. The work has been in charge of K. H. Logan of the Bureau of Standards, with three associates paid by the American Gas Association, the American Petroleum Institute and the Cast Iron Pipe Research Association. Prior to July 1, 1932, eleven men were working on soil corrosion problems at the Bureau. This year, as a result of the economy program, the force was reduced to four men including the two gas and oil technical associates. Altogether about \$350,000 has been expended on this work from 1922 to date, of which about 40 per cent was contributed by the Government. This is one of the most extensive cooperative corrosion investigations undertaken so far. Unless the work is continued, much of the investment will be practically wasted.

The following is a list of specimens that have been buried in connection with the Bureau of Standards soil corrosion investigations:

FROM 1922 TO 1932, INCLUSIVE		1929 AND 1930	
Ferrous metals.....	11,070	A.G.A. coatings.....	2,352
Nonferrous metals.....	6,820	A.P.I. coatings on pipe nipples...	2,070
Protective coatings.....	3,620	A.P.I. coatings on pipe lines.....	2,100
Miscellaneous.....	1,130		
	<hr/> 22,640		<hr/> 6,522

These specimens were buried in 49 typical soils at various sections of the country (for geographical location of the tests, see Fig. 113 of reference 5). The primary object was to determine the effect of soil corrosion independent of electrolysis due to stray electric currents. The results of this investigation may be summed up briefly as follows:

With respect to the influence of metal composition, Mr. Logan recently stated in one of his papers that "The data on underground corrosion indicate quite definitely, however, that all of the commonly used ferrous pipe materials corrode at nearly the same rate under the same soil conditions."⁽¹¹⁾ These data are summarized in Fig. 1.

The depth of pitting has been found to decrease more or less with time in most soils, as indicated in Fig. 2. The rate of soil corrosion has been generally correlated with the electrical conductivity in alkaline soils, and in some localities with the total acidity in neutral and acid soils, but

insufficient work has been done to predict with certainty the corrosiveness of any particular soil. However, definite progress has been made toward this objective and it would indeed seem to be a short-sighted policy for the Government at this time to curtail materially or discontinue the

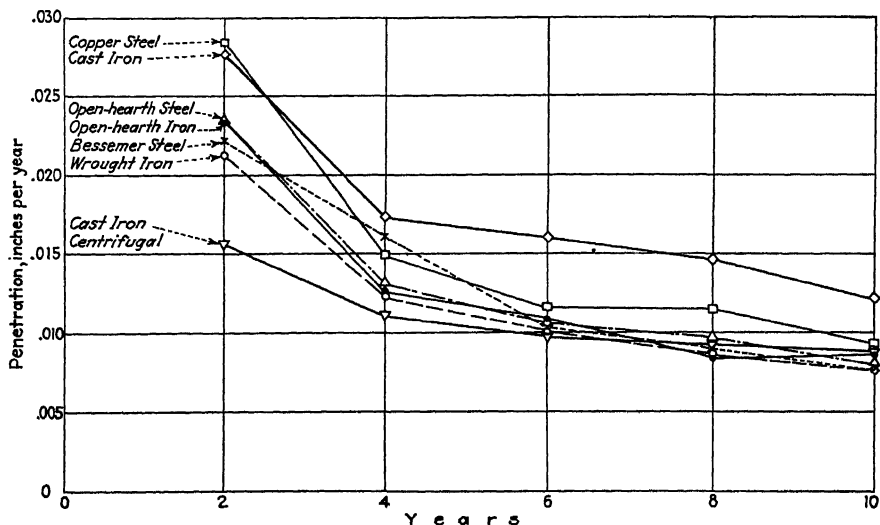


FIG. 1.—RATE OF PITTING VS. AGE OF PIPE (FROM BUREAU OF STANDARDS SOIL TESTS). WEIGHTED AVERAGE OF MAXIMUM PITS FOR EACH MATERIAL IN 22 SOILS.

support necessary for work on this problem, which is of such wide interest to the country at large.⁽¹²⁾

Extensive field tests of many types of protective coatings also have been carried out in typical soils by this cooperative organiza-

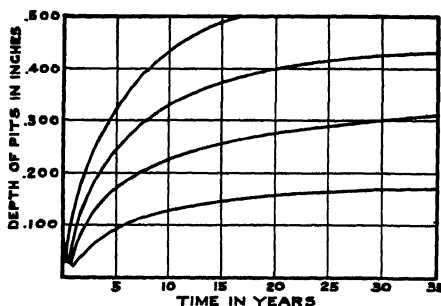


FIG. 2.—RATE OF PITTING VS. TIME IN VARIOUS SOILS (CONDENSED FROM PAPER BY GORDON N. SCOTT, AMERICAN PETROLEUM INSTITUTE, OCT. 26, 1933).

tion. Certain soils have been found to cause serious damage by distortion of soft bituminous coatings. As this type of coating has been used most generally, it appears that much money and material have been practically wasted for lack of information on the effect of various soils on pipe-coating materials. Bituminous coatings should be at least $\frac{1}{8}$ in. thick to be most effective and should be stiff enough, or protected from contact with soil

by suitable shielding material, to prevent distortion by soil stress. During the past two years the materials and methods of applying coatings to pipe have been radically improved and I believe it is now safe to say

that coatings capable of giving the protection desired under most soil conditions are now available at reasonable cost. Portland cement aggregates have long been used successfully for protection of pipe underground. A centrifugal method has been developed recently for the application of such material to the inside and outside of pipe to a thickness of $\frac{1}{8}$ to $\frac{1}{2}$ in. or more.

Cement has been used for 60 years on a limited scale for the lining of domestic water pipe. The use of this material is rapidly extending both for prevention of corrosion and for maintaining the carrying capacity of pipe. Some trouble has been caused by the increase in alkalinity of water in contact with new cement. To correct this condition, a portland cement mixture was recently developed in our laboratory that has about one-third the solubility of ordinary cement in water. This material is applicable particularly to the lining of water-storage tanks and water pipe.

The economics of underground pipe protection should be based on reliable data as to the useful life of bare pipe (allowing a small annual maintenance charge) compared with the life of similar pipe under the same conditions with various coatings. A pipe line company is usually not justified in spending much more for protection than would have to be set aside with compound interest to maintain the line perpetually, therefore the coatings must be comparatively low in cost except in very corrosive soils, where it may pay to spend as much as the original cost of the pipe to secure satisfactory life.

Underground pipe systems and electric cables have also been protected from ordinary soil corrosion and electrolysis, in limited areas, by lowering the electric potential of the pipe with respect to the earth, so that a current is continually impressed on the pipe from the surrounding soil. Since most of the damage on bitumen-coated pipe is at small breaks in the coating, it is more economical of electric power to first apply a bituminous coating of moderate thickness (about $\frac{1}{16}$ in.) to pipe that is to be protected by "forced drainage," or "cathodic protection," as it is usually termed.⁽¹³⁾ This method of protection is most economical and effective in restricted areas where the soil has a relatively high electrical conductivity. For instance, it is employed with satisfactory results to protect the underground gas system in New Orleans.⁽¹³⁾

Building Up Corrosion Resistance of Metal

With respect to the third method of prolonging the life of steel by increasing the resistance of the metal to the attacking media, here again for economic reasons it is very necessary to consider the increase in first cost, against the additional life, reduction of maintenance costs, and losses that may result from failures in service. In other words, the cost of corrosion-resisting ferrous alloys should be based upon the service obtained per dollar invested and not just upon the actual cost of the

alloy. The estimated life of the metal need not exceed the useful life of the equipment by a large margin, so that in selecting the most economical metal or other means of protection good judgment is required in the light of all the facts.

Only a few elements (such as chromium, nickel, copper, silicon and aluminum) have been found to increase the corrosion resistance of iron. Of these chromium is most generally effective under oxidizing conditions. Other elements that have not been used so generally in ferrous alloys may be found to add to the film-building power of the metal in other environments.

In the atmosphere the addition of 0.25 per cent copper will usually double or treble the life of steel and the addition of 1 per cent chromium with copper will about double the life again and at the same time add nearly 50 per cent to the strength of the steel, so that in this case the weight and thickness may be reduced materially for certain purposes. Low-alloy steels of this type are finding a wide field of use for roofing, parts of railway cars, and other exposed structures.

Steel cars sometimes deteriorate rapidly from corrosion. A reported analysis of car repair expenditures shows that rusting is responsible for 30 per cent of the total maintenance cost, which amounts to more than \$100,000,000 per year.* J. S. Unger made a comparative test in service on 200 freight cars, each constructed of one-half ordinary steel and one-half copper steel. At the end of 13 years the copper steel showed approximately 100 per cent longer useful life than ordinary steel, with less cost of maintenance because less frequent repainting was required. This should be a highly profitable field of use for copper steel or copper-chromium steel. About 9,000,000 tons of copper steel have been produced during the past 20 years. This represents on the average a potential increase of about 100 per cent in the life of steel where the coating fails and the bare metal is exposed to corrosive atmosphere (Fig. 3).

Unfortunately iron and steel carrying small amounts of copper, nickel, molybdenum, chromium or other elements have not proved sufficiently durable underground or immersed in water to warrant their more general use, but there is reason to believe that a low-cost ferrous alloy may be found that will come closer to meeting these requirements. Two or more alloying elements sometimes give a more stable film than one, but the evidence now available indicates that the happy union has not been found to meet these conditions. The number of possible combinations and the length of time required for testing make the investigation of compound alloys a slow process. Furthermore, it is necessary to develop the pretreatment that will give the lowest rate of attack and the minimum tendency to pit for any particular environment. The

**Iron Age* (Oct. 12, 1933) 13.

influence of chromium on the rate and distribution of corrosion of steel in warm Pittsburgh city water is illustrated in Fig. 4. Under such conditions and within the range of composition included in this test apparently steel with about 3 per cent chromium is preferable. The necessity for determining the maximum penetration as well as the average penetra-

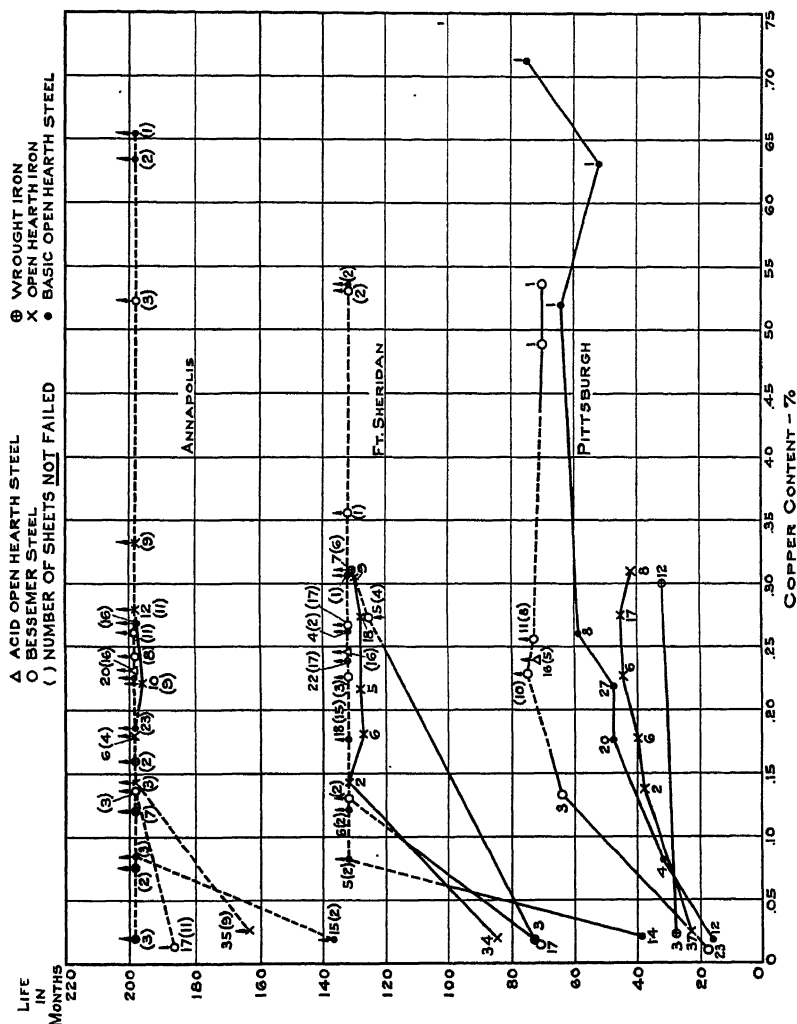


FIG. 3.—INFLUENCE OF COPPER ON LIFE OF STEEL IN ATMOSPHERE (FROM A.S.T.M. TESTS ON 0.22 GAGE SHEETS, PITTSBURGH, PA., FT. SHERIDAN, ILL., AND ANNAPOLIS, MD).

tion (by loss in weight) is also illustrated by this test. Similar charts are available for a few other single additions and others are under preparation for combinations that seem to contribute the best film-building properties. These tests will have to be repeated under three or four different conditions, and then the final answer should be obtained by test of the best of these alloys in service before definite conclusions can be drawn.

Prominent in the low-alloy class of corrosion-resistant steels is the 4 to 6 per cent chromium type, which lasts four to eight times as long as carbon steel in oil-cracking tubes and has therefore displaced a considerable amount of ordinary steel in such service during the past five years.

So much has been written recently on stainless and heat-resisting steels that it is not necessary to review this important development.⁽¹⁴⁻¹⁶⁾

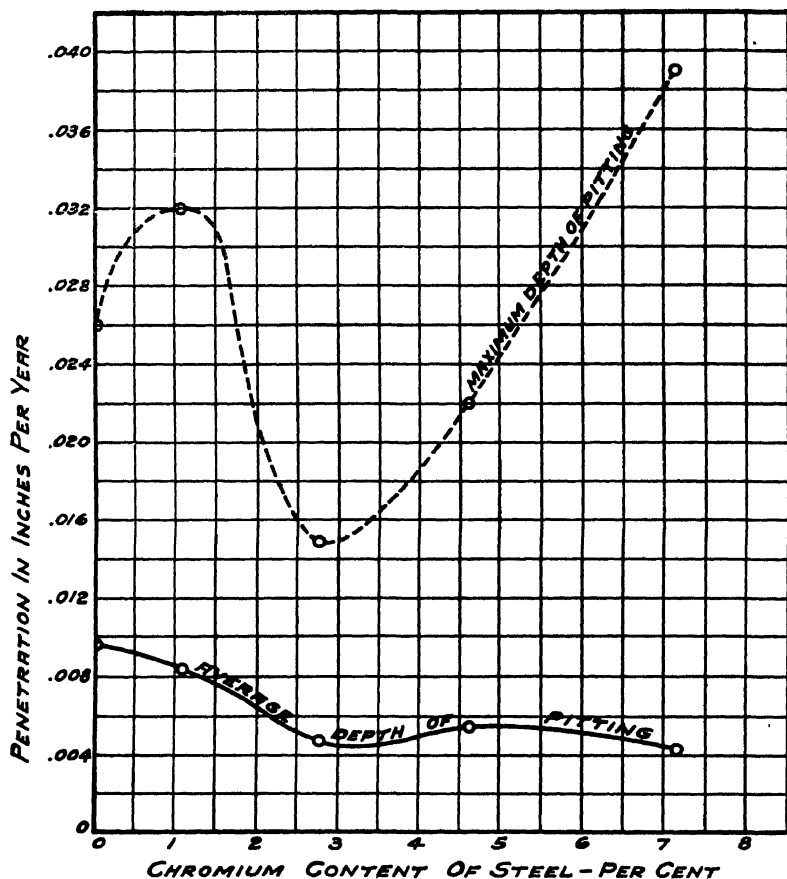


FIG. 4.—INFLUENCE OF CHROMIUM ON RATE OF CORROSION OF STEEL IN FRESH WATER. Penetration of corrosive attack in Pittsburgh city water at 140° F. aerated and having pH value of 6.8. Maximum depth of pitting plotted is average of deepest measurements for three specimens for period of two years.

Suffice to say that the tonnage of these alloys has shown a decided gain during the past few years in comparison with the total tonnage of electric-furnace alloy steels, as indicated in Table 4. We estimated that about 29,000 gross tons of stainless steel were manufactured in this country in 1933. This was mostly the 18-8 chromium-nickel type, and was rolled into sheets, plates, wire and pipe for use under severe atmospheric con-

ditions and in the chemical industries. Improvements and reduction in cost of the seamless process now make it possible to manufacture many of the ferrous alloys in the form of pipe. The modern process for manufacture of nitric acid by oxidation of ammonia was made commercially possible by the use of a large proportion of 17 per cent chromium steel in plant construction. Stainless-clad and nickel-clad steels are now available and for some purposes may prove as serviceable as the solid alloy.

TABLE 4.—*Comparative Tonnages^a*

Year	Electric-furnace, Alloy Steel, Gross Tons	Electric-furnace Stainless and Heat-resisting Alloy Steel, Gross Tons	Per Cent
1929	510,000	47,580	9.33
1930	300,500	53,080	17.60
1931	232,100	30,280	13.00
1932	140,870	23,770 ^b	16.80

^a *Iron Age* (Aug. 24, 1933) 11.

^b Estimated.

Corrosion-fatigue is produced by the simultaneous action of corrosion and stress and may be considered as a special form of notch-fatigue in which the notch instead of being formed mechanically is formed progressively by chemical attack accelerated by applied stress. There is probably a definite endurance limit for a mechanically notched specimen under ordinary fatigue, but in corrosion-fatigue, where chemical action continues, obviously there can be no fixed endurance limit, except under certain conditions of corrosion, and a certain number of stress cycles and time of exposure. Resistance to corrosion-fatigue increases with the specific corrosion resistance of the metal to the conditions encountered, other things being equal. Under some service conditions, where the rate of stress alternation is relatively slow, it has been found that high ductility of the metal is a significant factor in minimizing concentration of stress and in delaying or preventing the formation of the sharp crevices which appear as the first stage of corrosion-fatigue.

In general, the fracture of a metal part due to corrosion-fatigue may occur, at a stress far below the fatigue limit in the absence of corrosion, when the actual amount of corrosion is unbelievably small. For this reason it is particularly important to protect all parts that are subject to alternating stress, wherever practicable, even in an environment that is only mildly corrosive.^(17,18)

Any estimate of the value of the corrosion research work and preventive measures that have been applied during the past 10 years would necessarily be only a rough approximation at present, owing to lack of statistics. It is safe to say, however, that more has been accomplished

on the whole in that period than ever before, and that a wider and more active interest in this subject has been generated, which is bound to bring about practical results of permanent economic value.

In the oil industry, where corrosion waste was very apparent several years ago, the problem has received systematic study. A preliminary survey of conditions in the oil fields and refineries in 1927 indicated an annual loss due to corrosion of about 125 million dollars. In oil refining the saving due to protective measures has been estimated by engineers who have followed this problem closely at about 65 million dollars per year, which amounts to about one-half cent per gallon of gasoline produced. Several years ago this loss was figured as one cent per gallon.

The investigation of soil corrosion and protective coatings during the past five years has brought about almost a revolution in pipe line practice with reference to the problem of protection. Millions of dollars formerly spent every year on inadequate coatings are now being saved by omitting coatings where unnecessary and applying more suitable coatings where required.⁽¹⁰⁾

The solution of the manifold problems included in the general term "corrosion" is hastened by proper cooperation between the consumer, who knows the precise conditions to which he is subjecting the metal, and the producer, who is in a position to modify the properties of the metal supplied. The advance in our general knowledge of corrosion during the last decade is due largely to the great amount of cooperative work that has been done, particularly in this country, on corrosion testing and on means of lessening or preventing it in specific cases.

Special problems arising in a particular industry have been studied by groups of investigators directly connected with that industry; for instance, the American Petroleum Institute, the American Society of Refrigerating Engineers and the Bell Laboratories of the American Telephone and Telegraph Co. have done notable work in their respective fields. Steel manufacturers have also accomplished much in developing more resistant metals and better means of prevention. More general problems have been studied extensively by committees of the American Society for Testing Materials, on which both consumers and manufacturers have been represented. This work has gone on for a number of years, and is being actively continued. The cost, which has amounted to a considerable sum, has been in part defrayed by money contributions aggregating \$30,000, but principally by the contributions of the cooperating companies in terms of time of their men and of material supplied for the tests.

Many societies and organizations have committees on corrosion, more or less actively engaged on investigations of one kind or another; these, however, are not always as well coordinated as they might be. The steel industry as a whole has no general committee, such as the Committee on

Corrosion sponsored by the Iron and Steel Institute and Iron and Steel Manufacturers of Great Britain,⁽¹⁹⁾ but many of its units, as I have said, are taking an active part in work on corrosion. The present system is producing results with probably the least amount of organization but it seems desirable that there should be a national group representing those who are engaged on special industrial work to encourage and sponsor scientific research on fundamental problems relating to corrosion. These problems should be defined and assigned, with adequate financial support, to the men who are best able to carry on the work. The nearest approach to such organized effort that we have at present is the association of the oil and gas interests and the pipe manufacturers with the U. S. Bureau of Standards on soil corrosion, previously referred to. It seems that the American Institute of Mining and Metallurgical Engineers and other national societies should lend their influence and endeavor to secure more general support and better coordination of scientific work on this problem.

In Europe an International Mixed Committee was organized several years ago, including representatives of water, gas, and underground electrical communication interests, and is reported to be doing effective work on matters pertaining to the corrosion of underground pipe and cables. In America a few similar groups have been organized locally. Evidently the public utilities recognize the importance of this problem and the need for cooperative action.

Last September at an International Conference on Corrosion held in Chicago under the auspices of the Electrochemical Society, a considerable amount of overlapping and duplication of research work was apparent. The suggestion was made by one of the foreign contributors that a plan for international cooperation on some of these problems might be developed to advantage. No figures are available as to the total amount of money and time now being spent on corrosion problems in general, but it must be a very considerable sum. However, a relatively small part has been devoted to the scientific study of corrosion in this country.

Evidently much more remains to be done and, as in research that affects public health, the results are of such general and practical use to all that we should do our share in the study of the fundamentals in order that corrosion prevention may be put on a sound scientific basis as soon as possible.

The study of the formation, structure, and protective properties of metal surface films and the nature of their bond to the metal is one phase of this problem, the solution of which may be of far-reaching importance, for corrosion is usually a problem in surface reactions. To afford permanent protection it is, of course, essential that films be self-healing when injured. This is another property that requires more investigation. Further study of protective metal films may also help to produce better

artificial coatings. For instance, the failure of paints and certain metallic coatings usually starts at pinholes. In certain environment small imperfections in coatings have been found clogged with corrosion products, and in such cases the coating has shown a much longer life. It has been suggested that the bare metal and coating material may perhaps be designed so that the initial corrosion products will seal discontinuities in the coating.⁽⁶⁾ This principle suggests another field of promising research.

Relatively little has been accomplished in testing and improving paint materials for use under water. Standard methods of testing should be formulated and exposure tests started, as was done 25 years ago by the American Society for Testing Materials in connection with its investigation of paints for atmospheric service. If the average life of all paint were increased 25 per cent, it would mean a saving in this country of about 100 million dollars per year.

The foregoing examples serve to illustrate a few, but only a few, of the larger problems still awaiting solution in this important field. Obviously much remains to be done, but with the better understanding of these problems, resulting from the work accomplished within the past 10 years, we have reason to feel confident that ways of overcoming the onset of corrosion will be found that will enable us to utilize the valuable properties of steel in places where it now gives trouble because of corrosion.

Looking backward, we have much cause for encouragement, as practical means of protection have already been found for most cases where steel is vulnerable. I feel sure we will agree that if Professor Howe were with us this afternoon he would be the first to congratulate the metallurgists and other investigators of this generation on what has been accomplished and would point out in stronger terms than are at my command the necessity for pressing forward to a clearer understanding and better solution of the corrosion problem.

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Recent Trends in Blast-furnace Operation and Design*

By B. J. HARLAN,† LACKAWANNA, N. Y.

THE trying times experienced by the steel industry during the past four years have emphasized the necessity of producing pig iron at the lowest possible cost. The trend in both design and operation of blast furnaces has been toward this end rather than toward securing maximum production from a unit or group of units. In the following discussion the trend in design of stacks and auxiliary equipment will be taken up before operation is considered.

Although few furnaces have been constructed in the past few years, the trend is definitely toward larger furnaces with a hearth diameter of 24 or 25 ft. Such a furnace is very flexible, being able to produce efficiently any desired daily tonnage between 500 and 1000 or more. The detail of the design of furnace stacks, with the exception of the top, has changed little in recent years.

To decrease the velocity of gas through the throat of the furnaces, thereby reducing flue-dust losses, the stock-line areas are constantly being made larger. The top dimensions of the larger furnaces are usually as follows: Stock-line diameter, 19 to 20 ft.; large bell diameter, 14 to 15 ft.; straight section of throat, 5 to 10 ft. high; inwall batter, 1 to $1\frac{1}{4}$ in. per ft. The ratio between the area of the stock line and the area of the large bell is usually about 1.85 to 1. The stock-line diameter of some smaller furnaces has been increased to that of the hearth diameter of the stack at the expense of the stack batter.

Remarkable decreases in flue-dust production are claimed for the so-called "Venturi top," which is achieved by flaring the stock line, in the form of an inverted cone, from a diameter of 17 ft. at 10 ft. below the large bell closed to a diameter of 19 ft. 6 in. at 3 ft. below the large bell closed. Time alone will tell which of the two designs is the better. Because of differences in raw materials, one top may be better for some plants and the other top for other plants.

In the search for lower costs and higher efficiencies all operators are adopting stoves that will maintain maximum hot-blast temperatures with a minimum gas consumption. To meet these requirements, stove capacity of approximately 7 sq. ft. of heating surface and 1.8 cu. ft. of brick volume is required per cubic foot of wind blown per minute.

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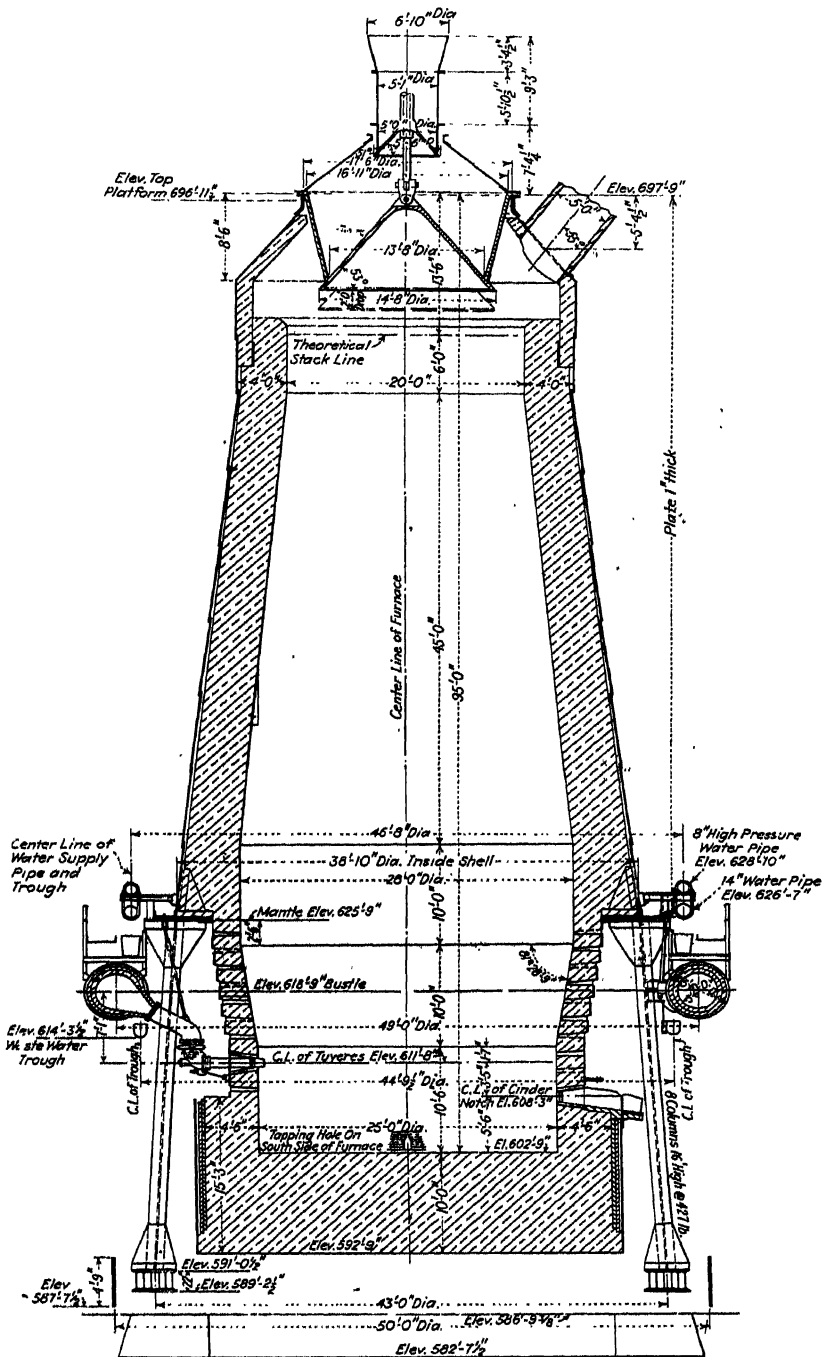


FIG. 1.—CROSS-SECTION OF A MODERN LARGE BLAST FURNACE.

other uses, 69 per cent. At plants using modern high-pressure blowers, the gas balance is about as follows: hot stoves, 20 per cent; steam for blowing, 21 per cent; and other uses, 59 per cent.

Few radical changes have been made in furnace auxiliary equipment recently. The trend is definitely toward larger iron and cinder ladles. Iron ladles handling 100 to 160 tons are universally used as well

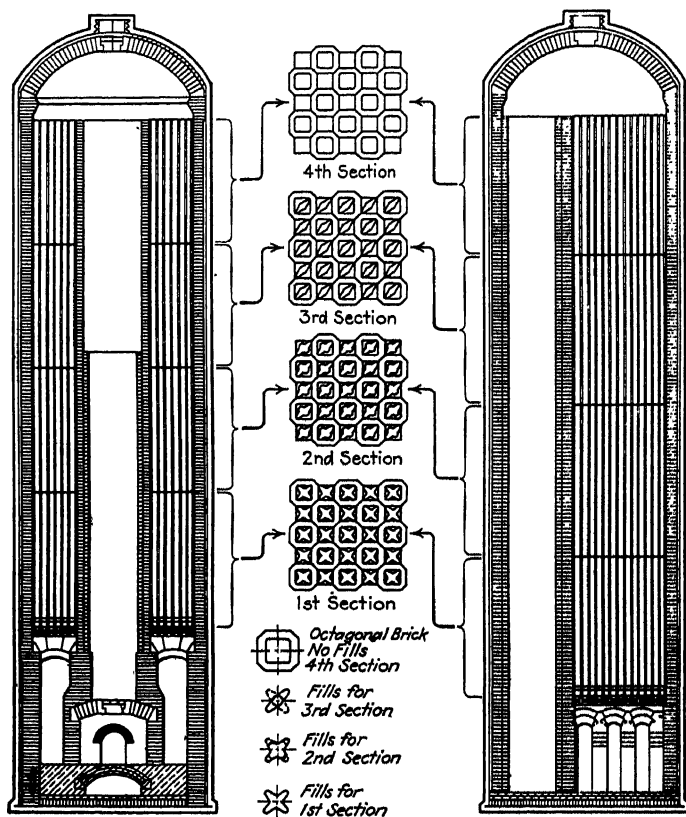


FIG. 4.—CROSS-SECTIONS OF A MODERN HOT STOVE.

as 400-cu. ft. single or double-pot cinder cars. When steam-driven turboblenders are used, the trend is toward higher steam pressures and superheat, with the resultant greater economy of operation. Several types of clay guns are in general use which obviate the old practice of taking the wind off the furnace after each cast to close in the tapping hole.

Owing to the variable demand for tonnage during the depression of recent years, a great deal has been learned about blowing furnaces. Many operators have decreased the normal wind blown on their furnaces by half

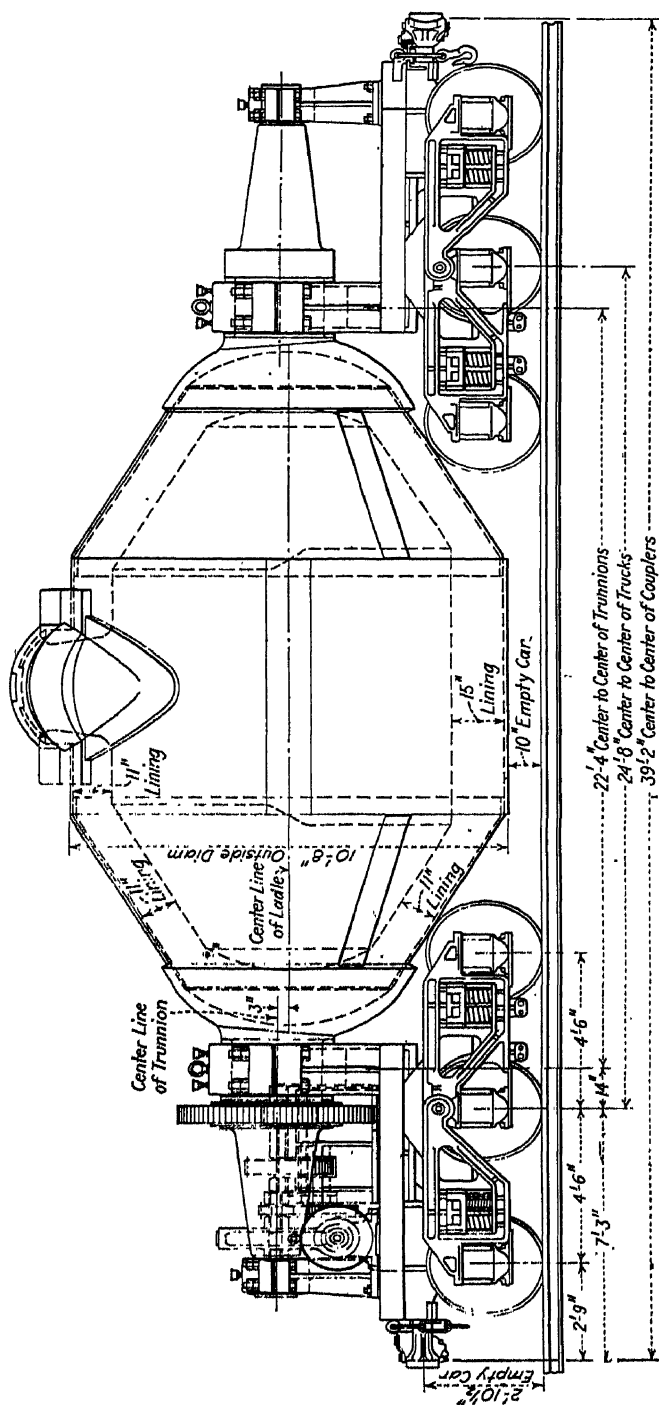


FIG. 5.—AN IRON LADLE OF THE MIXER TYPE.

or more, with a corresponding decrease in tonnage, with remarkably successful results. Other furnaces have been operated successfully on a daily intermittent schedule to meet the reduced demand for pig iron and gas. A furnace has been found to work equally well whether blown with 70 or 140 cu. ft. of wind per min. per sq. ft. of hearth area. This permits great flexibility in operation, especially on a large furnace.

Out of this low blowing, and variations in demand for tonnage, a practice has been developed that I call moderate blowing. I believe a more efficient operation can be obtained by blowing about 130 cu. ft. of wind per min. per sq. ft. of hearth area than the 150 cu. ft. that was commonly blown before the depression. With this rate of blowing, the reduction in flue-dust losses and fuel consumption more than offsets the additional tonnage that can be produced with a higher rate of blowing.

More emphasis is being paid all the time to sizing raw materials. Stone is usually well screened and sized to pass a $2\frac{1}{2}$ to 5-in. screen. Coke is generally crushed to 4 or $4\frac{1}{2}$ in. at the coke ovens and screened to the following sizes: $2\frac{1}{2}$ to 4 in., $1\frac{3}{4}$ to $2\frac{1}{2}$ in., 1 to $1\frac{3}{4}$ in., and $\frac{3}{4}$ to 1 in. The largest size is used in the furnaces. The smaller sizes are generally sold for domestic use. When there is no demand for domestic coke, or for any other reason it is desired to use the sizes larger than 1 in. in the furnaces, much better results can be obtained by charging the sized coke, in layers, in certain predetermined percentages than by charging unsized run of oven coke.

Excellent work is being done on crushing and sizing southern and other hard ores, with beneficial results in furnace practice.

Some sintering of Lake ores is being done on the Ranges. The furnace practice with these sintered ores is good. In the search for a cheap burden during the past few years, much attention has been paid to sintering stockpiles of flue dust. One plant has dredged 350,000 tons of sludge from the lake, mixed this sludge with its current production of flue dust, sintered this material and used it in the burden with good results. Other plants have sintered a mixture of stock flue dust, current dust, and Mesabi ore screenings and used the sinter produced from this mixture in quantities as great as 100 per cent of the burden, with excellent results.

Use of open-hearth slag in lieu of fluxing stone in the burden has come into almost universal use. In most plants the use of this material is limited only by the desired phosphorus content of the basic pig iron.

All the above-mentioned methods of sizing and sintering raw materials have enabled the furnace operators to use higher hot-blast temperatures with excellent results in fuel economy. Today, 1300° to 1400° hot-blast temperatures, or even higher, are common.

Summarizing briefly the above presentation, the present-day trend in furnace design and operation is as follows:

1. Big furnaces.
2. Large stock-line areas.
3. Well cleaned gas.
4. Efficient hot stoves.
5. Moderate blowing.
6. Sized raw materials.
7. High hot-blast temperatures.

The combination of these important factors enables the operator to produce a quality product at the lowest possible cost, which has always been the aim of the blast-furnace fraternity.

Basic Open-hearth Bottom-cast Practice and Iron-oxide Control

BY W. J. REAGAN,* OAKMONT, PA.

(New York Meeting, February, 1934)

A SURVEY of the literature on bottom-cast practice gives but scant information as to some of the real facts concerning this most interesting method of steel manufacture, and some of the information available is very misleading.¹

An exceptionally good description of this method of pouring or teeming is to be found in an English publication² on the heterogeneity of steel ingots. Quoting from this paper:

(a) With bottom teeming, the metal rises steadily and progressively in the mold with the minimum possible agitation, the main force of the stream coming from the ladle being broken down or retarded by the down gate or runner. Further, the stream of metal from the ladle, under these conditions of casting, is invariably maintained at a much more continuous rate and is steadier than with top teeming. (b) In view of the facts referred to in (a) it follows that with bottom teeming the metal is not exposed to atmospheric oxidation to anything like the same degree as with top teeming.

In this paper it is intended to detail briefly some of the advantages of bottom-cast practice and to discuss the possibilities of iron-oxide control in the basic open-hearth furnace. A description of the type of charge, ingot mold set-up, etc., is found in detail in an earlier paper.³

DESIGN OF INGOT MOLDS

In any kind of steel manufacture, ingot-mold design is important. L. H. Nelson⁴ lists in the order of their probable importance the following factors as influencing most the solidification of the ingot:

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* Open Hearth Department, Edgewater Steel Co.

¹ For instance, see E. C. Bitzer: Bottom Cast Practice. *Blast Furnace & Steel Plant* (December, 1931).

² Fourth Report on Heterogeneity of Steel Ingots. Iron and Steel Inst. (1932) 91.

³ W. J. Reagan: Practical Observations on Manufacture of Basic Open-hearth, High-carbon Killed Steel. *Trans. A.I.M.E.* (1930) 90, 45.

⁴ L. H. Nelson: Solidification of Steel in Ingot Molds. *Trans. Amer. Soc. Steel Treat.* (Oct., 1933).

1. Type, shape and size of mold.
2. Temperature of steel above its melting point.
3. Analysis of steel (due to difference in heat conductivity).
4. Temperature of mold.

This seems to be a logical presentation of facts relating to ingot solidification, listing of prime importance the type, shape and size of ingot mold. Incidentally, Nelson's paper contains much food for thought on the subject of ingot solidification.

In the selection of an ingot mold the first requisite is that it must be of suitable design for economical manufacture of the product to be forged or rolled from the ingot produced. For our type of work a twelve-sided, fluted mold is used with variations in diameter from 8 to 30 in. The mold length is standard for all diameters, 88 in. inside. The hot-top length with this kind of ingot is about 14 in. The mold has just sufficient taper to allow the ingot to be stripped from the mold, which is of the closed-bottom type. The taper is approximately 1 in. in 88 in. The ratio of mold weight to ingot weight is approximately 1.75 to 1.00. Considerable variation in mold weight is possible with but slight change in ingot structure. Mold weight has a very definite effect upon mold life, and for a given analysis mold life increases markedly as mold weight is increased. For example, by increasing the weight of a 21-in. diameter ingot mold from 12,000 to 16,000 lb., or about $33\frac{1}{3}$ per cent, the mold life is increased about 40 per cent. Ingot-mold life can also be increased by control of mold analysis and by the method of casting. Direct metal molds give a greater life than do cupola metal molds, but cannot compare with the cupola molds when extreme accuracy is desired on interior dimensions. Probably this is due to better control of casting temperatures, as metal direct from the blast furnace is apt to vary over a greater temperature range than metal from the cupola.

The most important factor in ingot-mold analysis, as regards mold life, is apparently manganese. As the manganese content of the mold is increased, the mold life also is materially increased. Silicon also seems of considerable importance, but its effect does not seem to be so constant as manganese, an increase in silicon not always producing an increase in mold life. There are so many variables to be taken into consideration in attempting to correlate mold life with metal analysis that it is almost impossible to make any hard-and-fast rules as to mold analysis. However, it can be stated that generally as the manganese and silicon contents of the mold metal is increased the mold life is increased also. To just what limits these figures can be carried is not known, but in ordinary commercial practice it is possible to obtain ingot molds with a manganese content of about 2.00 per cent and silicon content in the neighborhood of 1.75 per cent.

POURING PRACTICE

It has been shown in a previous paper⁵ that pouring practice is of vital importance to steel casting, the proper pouring procedure depending upon the type of steel being made, upon the type of mold and upon the temperature of the molten steel. By proper control of pouring speed, which actually means pouring temperatures, it is possible to obtain ingots (either bottom-cast or top-cast) free from cracks, either circumferential or longitudinal, and with proper hot-top equipment an ingot entirely free from excessive piping can be obtained. The hot top should represent 9 per cent or less of the total weight of the ingot, and the ingot yield should be about 90 per cent. Bottom-cast ingots can be produced commercially in any size. Thousands of tons have been produced within the writer's experience ranging in weight from 1000 to 50,000 lb. These do not by any means cover the minimum or maximum weights that it is possible to produce commercially by the bottom-cast process but are only the limits produced within the writer's actual experience, and these limits have only been established by the size of ingot necessary to produce the proper size of forging necessary for making the finished product desired.

Bottom-cast ingots are noted for their freedom from pipe. In 1927 about 15,000 tons of Krupp rails were imported into this country, all made by the basic open-hearth bottom-cast process. In a report of inspection on these rails made by a nationally known firm of engineers, not one single piped rail was listed for the 15,000 tons tested, and to obtain this freedom from piping there was no excessive cropping necessary.⁶

In addition to high ingot yield an additional advantage of bottom-cast practice is the usual above-normal life of ingot molds. A typical 20-in. diameter mold of the type just described, used in bottom-cast practice, should give an average of 150 heats per mold, or roughly 600 net tons of ingots per mold. It is not at all uncommon to find molds with a life well over 200 heats. Better control of pouring speeds is one of the probable reasons for this long life.

CLEANLINESS OF BOTTOM-CAST INGOTS

Much has been written about the cleanliness of top-cast steel as compared with bottom-cast steel. In a study of the nonmetallic content of ingots made by the basic open-hearth bottom-cast process many interesting data have been assembled.⁷ A number of ingots have been sampled and the cleanliness of the steel determined by the Dickenson

⁵ Reference of footnote 3.

⁶ C. W. Gennet, Jr.: *The Iron Age* (Apr. 14, 1927).

⁷ C. H. Herty, Jr. et al.: Deoxidation of Steel with Silicon. *Bur. Mines Tech. Paper* 492.

method.⁸ Samples were taken from each ingot as indicated in Fig. 1. Each sample was composed of about $\frac{1}{2}$ lb. of cuttings, and was quartered repeatedly until a sample of standard size was obtained. The cuttings were obtained while the ingots were being sliced in a lathe and represent an average sample or ring of metal removed from three sections of varying depth from just underneath the ingot skin to almost the center of the ingot. These three samples were also taken from three planes of the ingot, just beneath the hot top, about the middle of the ingot and from a point about 14 in. from the bottom of the ingot.

The drawings in Fig. 2 represent 9 or more samples from various portions of the ingot, which, as can be seen from Fig. 1, are truly representative of the interior of the ingot. No attempt will be made to discuss the accuracy of the Dickenson method for obtaining total silicates, but it is believed that for this type of steel the SiO_2 content as determined by this method is an accurate indication of the amount present in the steel.

Ingot A is from a heat of steel in which a special method of deoxidation was used. This ingot is somewhat cleaner than any of the others shown, the average percentage of nonmetallics being 0.0089. The maximum nonmetallic content is near the top of the ingot, at a point halfway between the outside and the center.

Ingot B, C, D and E were all cast from the same heat. The average nonmetallic content of all is about the same, i. e.: ingot B, 0.0183; ingot C, 0.0182; ingot D, 0.0208; ingot E, 0.0187. There is a marked difference in segregation in the two sets of ingots, which probably is due to a difference in pouring speed or casting temperature, ingots B and C being cast

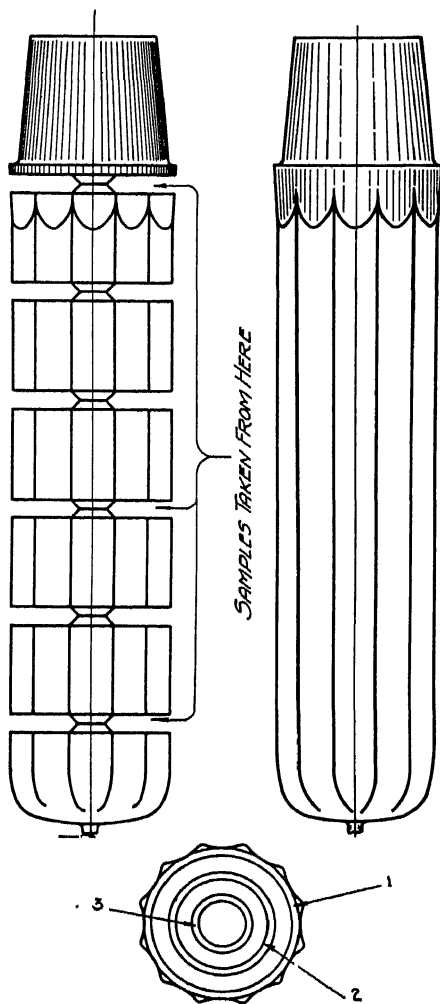


FIG. 1.—METHOD OF SAMPLING INGOTS.

⁸ *Jnl. Iron and Steel Inst.* (1926) **113**, 117 and *Carneigie Inst. Tech. Bull.* 37.

at a slightly lower temperature than were D and E. It is particularly interesting to note the similarity of segregation in ingots B and C, which were poured at the same temperature, the curves being strikingly similar.

The four ingots F, G, H and I were also all cast from the same heat, their average silicate content being very much alike, i. e.: ingot F, 0.0167; ingot G, 0.0159; ingot H, 0.0172; ingot I, 0.0136.

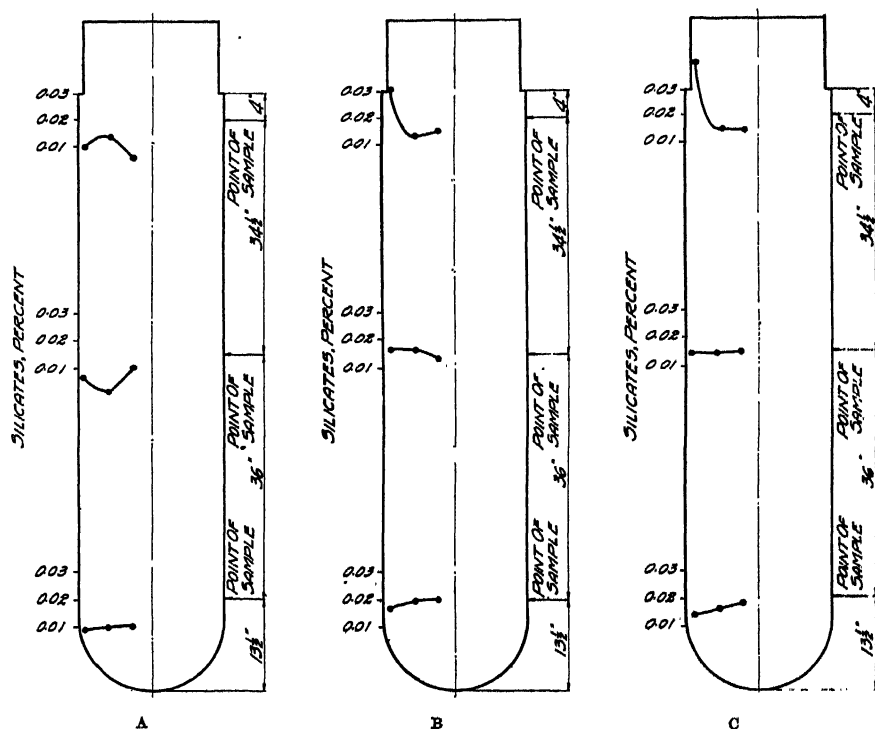


FIG. 2.—SEGREGATION OF SILICATES IN BOTTOM-POURED INGOTS.
Ingot A from heat 12422; ingots B and C from heat 12533.

The average analysis of the inclusions obtained from all of the ingots shown was as follows: FeO, 80.30 per cent; MnO, 4.60; SiO₂, 13.60; Al₂O₃, 2.25.

From the segregation results, it is believed that the segregation of silicates may be explained by a simple rejection of nonmetallic matter at the interface between liquid and solid steel and by the path that the particles follow in the liquid steel.

These figures and segregation curves are presented to show that it is possible to make steel by the basic open-hearth bottom-cast process with considerably less than a normal amount of nonmetallic inclusions. Some idea of the possibilities of a thorough study of nonmetallic inclusion segregation can be obtained from a study of the curves presented. Our

English friends have presented much that is of interest in this line in their presentations during the past few years of a study of the heterogeneity of steel ingots.

IRON-OXIDE CONTROL IN THE BASIC OPEN HEARTH

Iron-oxide control in the basic open-hearth furnace has long been the object of much research. It has been shown heretofore that the FeO content of the slag is largely influenced by the SiO_2 content of the slag. An earlier paper, showing this graphically,⁹ indicates that as the FeO

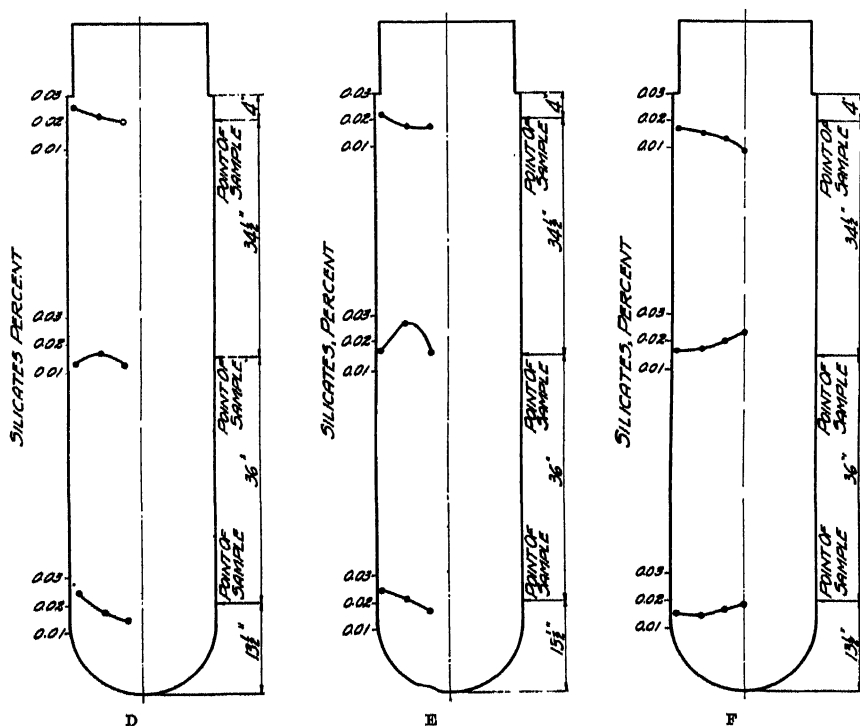


FIG. 2 (CONTINUED).—SEGREGATION OF SILICATES IN BOTTOM-POURED INGOTS. Ingots D and E from heat 12533; ingot F from heat 12501.

decreases the SiO_2 increases. In spite of the fact that SiO_2 has been known to be such an influencing factor in controlling the percentage of FeO in the slag, it has been a long, tedious job to find out just why this is so. The only element producing SiO_2 in the slag of a basic open-hearth furnace is silicon, either in the form of silicon in the charge or from silica contamination of the bath or slag.

⁹ W. J. Reagan: Some Effects of Temperature and Iron Oxide, etc. *Trans. A.I.M.E.* (1932) 100, 141.

The effect of adding silicon to the charge was first noted at this plant when ingot-mold scrap was used to replace part of the pig iron in the charge. Owing to the higher silicon content of the mold scrap as compared to the pig iron, the resulting increase in silicon in the charge was almost invariably reflected in higher SiO_2 in the slag and consequently a lower FeO . With these results in mind, Dr. Herty completed the picture in his recent investigation of FeO control.¹⁰

In the use of FeO control, it is essential to control both the silicon content of the charge and the amount of lime (CaO) in the charge.

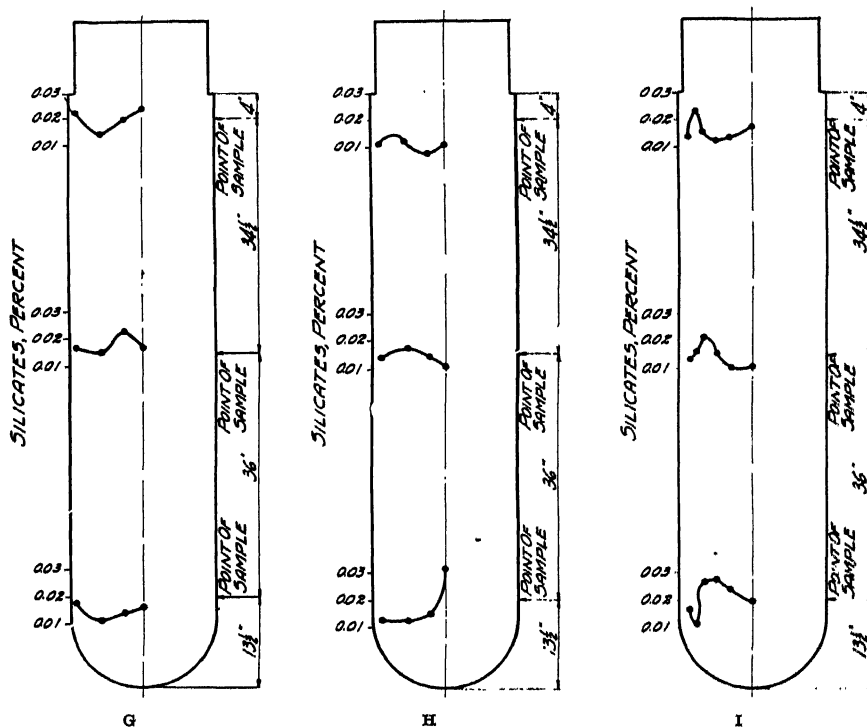


FIG. 2 (CONTINUED).—SEGREGATION OF SILICATES IN BOTTOM-POURED INGOTS. Ingots G, H and I from heat 12501.

Fig. 3 shows the effect of silicon in the charge upon the carbon at which a heat will melt. The silicon apparently has a greater effect upon the carbon at which a heat will melt than the carbon content of the charge itself. The carbon content of the heats shown on Fig. 3 varied from 2.20 to 2.34 per cent, a variation of only 14 points of carbon, while the silicon content varied from 0.57 to 0.68, but the carbon at melting varied from 0.94 to 1.48 per cent. The lime charge on all of the heats shown was practically the same. It is particularly interesting to notice the three

¹⁰ C. H. Herty: 20th Progress Report to Metallurgical Advisory Boards to Carnegie Institute of Technology, October, 1933.

heats on the graph, all with a silicon content of 0.64, and all melting within two points of carbon of one another.

By controlling the metalloid content of the charge, especially silicon, and keeping the lime charge at the lowest point, it is possible to obtain

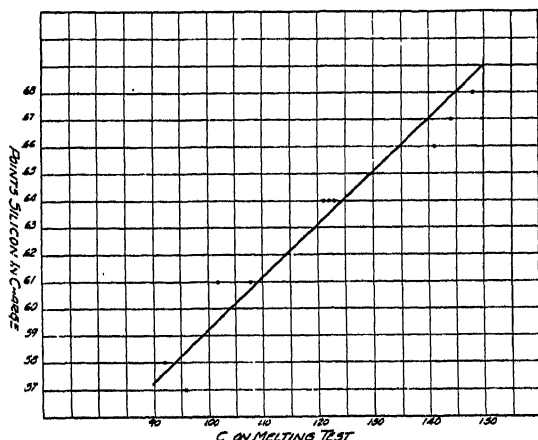


FIG. 3.—EFFECT OF SILICON IN CHARGE UPON CARBON AT WHICH HEAT WILL MELT.

almost complete removal of the FeO formed during the melting-down period of the heat. Any additional lime needed may be added just before the ore addition; to obtain the desired basicity or to avoid attack of the

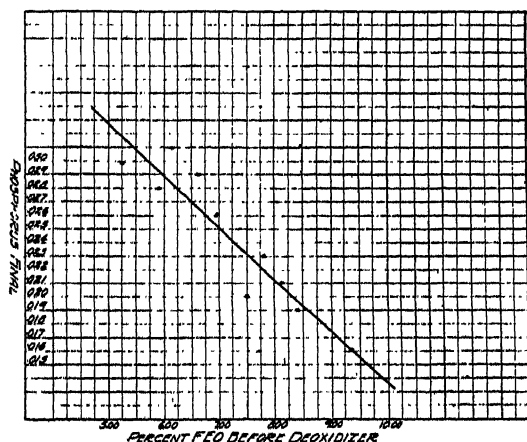


FIG. 4.—EFFECT OF FEO ON FINAL PHOSPHORUS CONTENT OF STEEL.

banks by a too siliceous slag. By controlling these items and also the fluidity of the slag, the FeO at the low point (to be described later) will be as low or lower than desired. After the ore addition has worked through the slag, FeO in the form of roll scale or fine iron ore may be

TABLE 1.—*Metal Analysis, Heat 24412*

Time, P.M.	Analysis, Per Cent				
	C	Mn	P	Si	S
2.50	1.99	0.23	0.076	0.024	
3.20	1.79	0.25	0.075	0.005	
3.50	1.44	0.28	0.076		
4.23	1.41	0.38	0.076		
4.50	1.27	0.44	0.077		
5.20	1.22	0.45	0.067		
5.42	1.17	0.45	0.056		0.026
6.06	1.11	0.44	0.051		0.024
6.26	1.06	0.36	0.037		
6.36	1.04	0.38	0.037		
6.46	1.01	0.38	0.035		
6.56	0.98	0.39	0.034		
7.07	0.95	0.40	0.033		
7.28	0.89	0.41	0.033		0.023
7.50	0.81	0.37	0.023		
8.13	0.72	0.38	0.019		0.023
8.27		0.46	0.016		
8.33		0.46	0.018		
8.48		0.55	0.019		

TABLE 2.—*Slag Analysis, Heat 24412*

Time, P.M.	Analysis, Per Cent							
	FeO	Fe ₂ O ₃	MnO	SiO ₂	P ₂ O ₅	CaO	MgO	Al ₂ O ₃
2.50	9.70	0.76	24.24	30.10	1.78	25.43	5.44	2.80
3.20	6.50	0.76	22.49	30.60	1.55	28.12	5.84	2.34
3.50	4.96	0.89	20.82	30.84	1.33	31.58	6.34	2.18
4.23	3.82	0.63	17.94	30.80	1.21	35.49	6.20	1.84
4.50	3.42	0.76	16.41	31.60	1.24	40.40	6.16	1.76
5.20	4.17	1.13	15.53	30.44	1.35	40.85	6.31	2.26
5.42	4.34	1.51	14.61	28.00	1.95	38.54	6.88	2.28
6.06	4.79	2.02	14.85	27.64	2.25	41.51	6.09	2.42
6.26	7.76	2.27	14.98	25.28	2.67	37.91	6.15	2.68
6.36	6.84	2.14	14.56	24.80	2.77	38.72	6.16	2.40
6.46	6.84	1.89	14.13	25.28	2.70	39.96	6.16	3.05
6.56	6.27	2.02	13.90	25.60	2.69	40.50	6.00	2.76
7.07	6.50	1.89	13.84	25.04	2.70	40.76	6.28	2.68
7.28	6.27	2.39	12.69	23.60	2.69	41.54	6.69	2.42
7.50	7.64	2.14	12.79	22.88	2.70	41.74	6.66	2.59
8.13	6.96	2.90	11.59	20.68	2.74	43.47	7.24	2.52
8.27	7.07	2.52	11.34					
8.33	7.18	1.89	11.58					
8.48	6.95	2.65	12.28					

added to the slag to increase the FeO to the desired amount, which is determined by the final phosphorus content of the steel. Some experimental work has been done in an attempt to reduce FeO in the slag after it has reached an amount higher than is desired, but as yet sufficient data have not been obtained to prove this method practical. Heats that are too high in FeO at the low point will finish high in FeO, while heats that are below the low point desired may be increased by additions of fine ore or roll scale to the slag. Fig. 4 shows the effect of FeO upon the final phosphorus content of the steel. For a given excess base or basicity of the slag the final phosphorus is determined by the FeO content of the slag; the lower the FeO, the higher the phosphorus.

Slag fluidity must be controlled to prevent FeO from building up in the slag during the lime boil, as the heavier slags cause the FeO to build up in them.

The following details are all for a typical FeO-controlled heat. Table 1 gives a complete analysis of all metal preliminaries from approximately three hours previous to the time the heat was completely melted until it was tapped. Table 2 gives a complete slag analysis for all slag samples taken at the same time the metal preliminaries were taken. Table 3 shows details of the heat, charge, additions, and so forth.

TABLE 3.—*Details of FeO-controlled Heat*

In Charge, Lb.	Working Heat, Lb.	Pig Analysis, Per Cent	Analysis of Charge, Per Cent
Total charge..... 180,000	Iron ore..... 250	C..... 4.47	2.43
Basic pig..... 87,500	Burnt lime..... 1,120	P..... 0.170	0.10
Scrap..... 92,510	Fluorspar..... 375	Mn..... 1.83	1.18
Burnt lime..... 2,010	Scale..... 1,200	Si..... 1.20	0.68
Limestone. 8,500		S..... 0.021	0.026

Time charge to tap, 11 hr. 30 min.

Start to charge 9:25 a.m.

Finish charging 12:00 noon

Tapped 8:55 p.m.

1200 lb. 50 per cent ferrosilicon added to ladle

Final analysis, per cent:

C	P	Mn	Si	S
0.76	0.022	0.68	0.28	0.021

Additions

5:42 p.m., 1020 lb. burnt lime

6:06 p.m., 400 lb. scale

6:10 p.m., 250 lb. lump iron ore

6:20 p.m., 400 lb. scale

7:32 p.m., 200 lb. scale

125 lb. fluorspar

7:35 p.m., 200 lb. scale

7:45 p.m., 250 lb. fluorspar

7:55 p.m., 250 lb. burnt lime

8:16 p.m., 1500 lb. spiegeleisen

250 lb. fluorspar

8:30 p.m., 100 lb. fluorspar

8:40 p.m., 800 lb. ferromanganese

Fig. 5 gives a graphic record of the heat from 3:00 to 8:20 p.m., or from 3 hr. before melting until tapping. It pictures strikingly the various reactions taking place during the progress of the heat, and from this graph a very pretty picture of a typical FeO-controlled heat may be obtained. We can see that silicon in the charge is eliminated early in the

heat, at 3:30 p.m., the metal sample showing 0.005 per cent silicon. The low point in FeO can be clearly seen at about 4:50 p.m., the analysis of the slag at that time giving 3.42 per cent FeO. This low point is about the middle of the lime boil and the extremely high SiO_2 content of the slag at this time, about 31.60 per cent, is also noticeable. This curve indicating the low point in FeO, approximately one hour before the heat is completely melted, is typical of all heats investigated, the same type of curve being found on over 30 heats. As the lime goes into

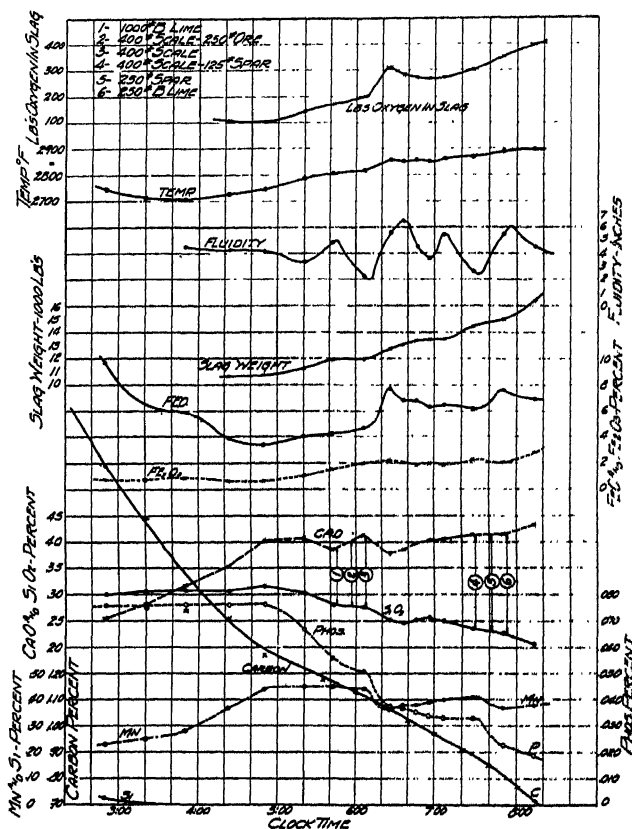


FIG. 5.—RECORD OF HEAT FROM 3 HR. BEFORE MELTING UNTIL TAPPING.

solution there is a gradual increase in FeO and CaO until just before the ore addition. After the ore addition the carbon is eliminated more rapidly and the phosphorus takes a decided drop due to the addition of FeO to the slag from both the ore addition and from the scale added at about the same time. At 6:06 p.m. the phosphorus was 0.051. Because the heat melted close to the final carbon (0.75 to 0.80) it was found necessary to add scale to the slag as the FeO possible to obtain from the very small ore addition (250 lb.) would be insufficient to reduce the phosphor-

us sufficiently to allow the heat to finish about 0.025 phosphorus. It was desired to finish the slag in this heat with FeO at about 7.00 per cent, which would result in a final phosphorus of approximately 0.025. How close the desired results were to the final figures can be seen, as the final phosphorus was 0.022 per cent and the FeO in the slag before deoxidation was 6.96 per cent. After the first ore and scale addition the phosphorus dropped from 0.051 per cent down to 0.037 per cent. This figure was still too high to allow the heat to finish at or below 0.025 phosphorus, so at 7:32 and again at 7:35 p.m. 200 lb. of scale was added to the slag. The immediate effect of this addition was to reduce the phosphorus to 0.019 per cent and the increase in FeO is clearly indicated on the graph of Fig. 5, finishing slightly under the desired 7.00 per cent.

The slag fluidity as indicated by the viscosimeter shows relatively the fluidity of the slag at any time during the progress of the heat. On Fig. 5 the effect of the ore addition upon decreasing the fluidity of the slag can be clearly seen. Fluidity control is important in the use of FeO control.

This, briefly, is FeO control. The SiO_2 in the slag is maintained at a high point by a high silicon content of the charge and by a minimum amount of lime in the charge. Control of the silicon and lime in the charge results in a low FeO before melting, which can be increased to the desired finishing FeO by additions to the slag of fine ore or roll scale. It will be necessary for each steelmaker to work up his own figures for using this method. The very thin siliceous slags resulting from the high silicon content of the slag prevents dissolving of the lime during the early part of the heat and accordingly prevents absorption of the FeO by the lime; as high lime allows for a greater pick-up of FeO, the heavier slags, because of the greater amount of lime in them, allows the FeO to build up. The average pick-up of FeO from the normal ore addition on the heats investigated was about 6.00 per cent. This figure is bound to vary in the different plants, depending upon slag conditions, type of iron ore, etc. Each plant must work out its own values.

In conjunction with the use of the FeO-control method it is essential that composite samples of slag be taken from at least three doors. It is also essential that the slag samples be taken from underneath the top layer of the slag. This layer is undoubtedly very thin, but if the slag samples are relatively high in Fe_2O_3 it is definite assurance that the sample has been contaminated with Fe_2O_3 from the top slag layer. The method used in taking samples from underneath the top layer is as follows: Allow the test spoon to be submerged under the top layer of the slag, the spoon being turned upon its side while passing through the top layer. As soon as it passes through the top layer bring it into an upright position, allowing the spoon to fill from the slag-metal line upwards. As

soon as the spoon is removed from the slag and out of the furnace allow the top layer of slag in the spoon to crust over for a few seconds, then punch a hole in the top crust and allow the contents to run out on a clean plate or sheet.

Effects of High Iron Oxide versus Low Iron Oxide

The following are a few reasons for striving to keep the FeO in the slag as low as possible for the type of steel being made.

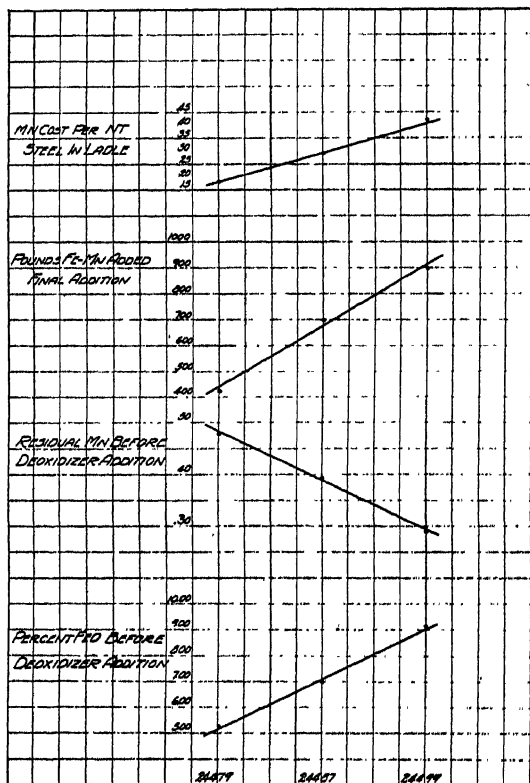


FIG. 6.—EFFECT OF HIGH AND LOW FeO UPON RESIDUAL MANGANESE IN BATH.

Fig. 6 illustrates the effect of high and low FeO upon the residual manganese content of the bath. For a given slag basicity and a given manganese content of the charge, the residual manganese is controlled by the FeO content of the slag and by the temperature of the bath; the higher the temperature, the higher the manganese content of the steel. On all three heats illustrated the manganese content of the charge was about constant and the temperature of the bath about the same. The marked difference in the residual manganese contents of the three heats

is noticeable. The heat with an FeO content of about 5.25 per cent has a residual manganese of about 0.48, while the heat with an FeO of about 9.10 per cent has a residual manganese of only 0.29 per cent. The resulting increase in cost due to low residual manganese is also plotted, the increase amounting to about 24 cents per net ton of steel in the ladle.

Fig. 7 illustrates the effect of high and low FeO upon the furnace loss and upon rejections. With an average FeO of 9.90 per cent, a furnace loss of about 8.20 per cent is indicated, while an FeO of about 6.80 per cent shows a loss of only 6.85 per cent. This reduction amounts to 1.35 per cent and is reflected in an increase in metallic yield of this 1.35 per cent and a decrease in rejections, also indicated upon the chart.

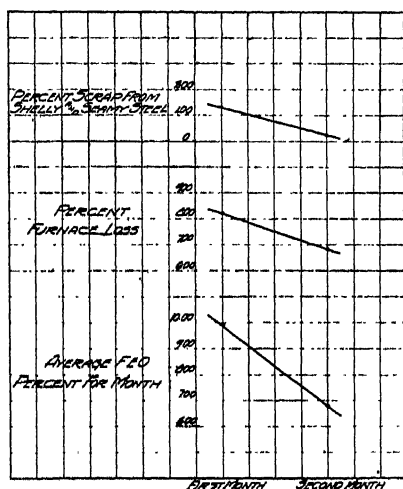


FIG. 7.

FIG. 7.—EFFECT OF HIGH AND LOW FeO UPON FURNACE LOSS AND REJECTIONS.

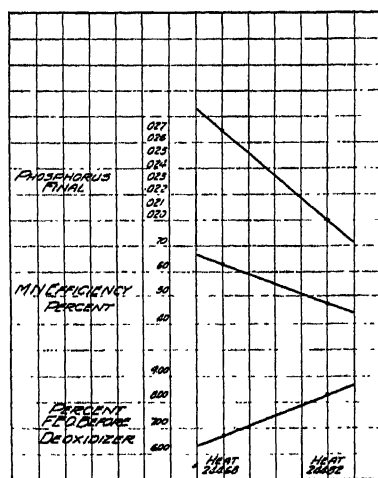


FIG. 8.

FIG. 8.—EFFECT OF HIGH AND LOW FeO UPON EFFICIENCY OF MANGANESE ADDITION AND EFFECT OF FeO ON PHOSPHORUS.

Fig. 8 illustrates the effect of high and low FeO upon the efficiency of the manganese addition and also the effect of FeO upon phosphorus. A low FeO content in the slag gives greater manganese efficiency than a high FeO content.

How the amount of lime in the charge affects the FeO content of the slag and also how it affects slag volumes makes an interesting study. Perhaps the most complete investigation of this subject has been described by C. D. King.¹¹ In his paper he shows that excessive slag volumes caused by too heavy lime charges increase costs and lower yields by lengthening the time of heats and increasing the pig charge with its attendant loss of metalloids and consequent lower yield.

¹¹ C. D. King: The Metallic Charge in Basic Open Hearth Furnaces. Amer. Iron and Steel Inst. (Oct., 1931).

ACKNOWLEDGMENTS

The author is indebted to Dr. C. H. Herty, Jr. and his associates for their assistance and everlasting enthusiasm.

SUMMARY

Basic open-hearth bottom-cast ingots can be produced commercially free from cracks, free from excessive pipe, with yields usually greater than that obtained from top-cast ingots. Basic open-hearth bottom-cast ingots can be produced with comparative freedom from nonmetallic inclusions.

Basic open-hearth iron-oxide control permits accurate control of the FeO content of the slag, with a resulting decrease in the cost of steel manufacture, due to greater efficiencies from additions, etc., and from higher yields and steel of better quality.

DISCUSSION

(L. F. Reinartz presiding)

J. E. CARLIN,* Massillon, Ohio (written discussion).—It is always pleasant to read a paper on steel manufacture that contains actual slag and metal analyses; Mr. Reagan's paper shows very clearly the change in metal and slag analyses as the heat progresses.

In the opening paragraphs Mr. Reagan refers to a paper published in 1932, in which he showed that the FeO content of the slag is largely influenced by the SiO₂ content. The paper also shows, graphically, that as the FeO decreases the SiO₂ increases. This information is interesting, because a strict interpretation indicates that the FeO content of the slag, after the heat has melted, may be decreased by adding silica.

The writer has always considered that high silica in the slag is the effect rather than the cause of low FeO. This opinion was reached as a result of the following theory: For a given charge of scrap and melting conditions, a definite weight of iron oxide is formed by oxidation of the scrap. When a given weight of pig iron with a definite weight of carbon, manganese, phosphorus and silicon is added, a certain amount of iron oxide is reduced—the amount depending mainly on the weight of silicon and carbon added. As the weights of silicon and carbon added increase, more iron oxide is reduced, and as a result the excess iron oxide or the amount that shows up in the slag analysis, decreases.

This reasoning supports the opinion that high silicon in the charge is the cause of low FeO in the slag, and that high silica is merely the effect. This point is important, because as a result of the opposite opinion, it is common practice to include lime when adding ore.

The charge details were interesting—it would be very much appreciated if Mr. Reagan would describe the type of scrap used and advise if it is uniform from heat to heat. It would be interesting to know also if the pig-iron analysis is held to fairly close limits.

The paper brought out one very important point in connection with the relation between phosphorus removal and FeO content of the slag. The data show that

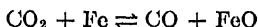
* Assistant Chief Metallurgist, Union Drawn Steel Co.

approximately 180 lb. of phosphorus was present in the charge, and that although only 4.80 per cent FeO was present before any scale was added, it was necessary to increase the FeO percentage of 7.00 in order to reduce the phosphorus content below 0.025 per cent. The manganese efficiency on the heat was only 62 per cent, which indicates that the FeO content of the slag would have to be very low to get real high efficiency.

Mr. Reagan did not mention temperature, and advice on this point would be interesting, in view of the fact that the phosphorus elimination reaction is exothermic.

The CaO content of the finishing slag seemed to be low, when the high silica content and assumed high quality desired are considered. The remarks regarding the reason for the minimum of lime charged were not very clear, especially the following: "The very thin siliceous slags resulting from the high silicon content of the slag prevents dissolving of the lime during the early part of the heat and accordingly prevents absorption of the FeO by the lime; as high lime allows for a greater pick-up of FeO, the heavier slags, because of the greater amount of lime in them, allow the FeO to build up." The probable explanation of the "greater pick-up of FeO" when high lime is used, is the oxidation of iron by the CO₂ resulting from the calcination of the stone. This point could be checked by charging burnt lime only. In view of the fact that the permanent removal of phosphorus depends upon an excess of FeO and CaO at all times, it would be logical to carry as high a lime content as possible, especially on high-silica slags when the available base is comparatively low.

It is logical to believe that the FeO formed from the reaction



would not exceed 1200 lb., and for that reason the amount of lime charged should not be important because it was necessary to increase the FeO percentage by adding 1200 lb. of scale.

W. J. REAGAN (written discussion).—In replying to Mr. Carlin's question, I feel that the low FeO content of the slag is entirely due to the high SiO₂ content of the slag, which is caused by the high silicon content of the charge. This fact can readily be seen by varying the silicon content of the charge and noting the resulting variation of the SiO₂ content of the slag.

Manganese efficiency is controlled by several factors: by the FeO content of the slag, plus the time in the furnace plus the amount of ferromanganese added, the larger the amount added the greater being the efficiency.

The temperature of the heat mentioned was undoubtedly on the cold side, the temperature (pouring) being about 2810° F. and the ladles having a skull of about 800 pounds.

I can see no connection between the CaO content of the finishing slag and the reference to assumed high quality. We do know that the higher the FeO in the finishing slag the greater amount of dirt we will find in the steel. The final FeO is determined by the final phosphorus desired. If the CaO content is high enough for a given FeO to allow the heat to finish at the desired phosphorus content, the quality will be all right.

A low lime charge naturally produces a slag high in SiO₂, which is thin and fluid, and low in FeO. The fluidity of a slag has a great deal of effect on the diffusion of FeO from slag to metal. We have found that with heavy slags, usually with a greater amount of excess CaO, the FeO builds up in the slag and consequently in the metal. A high-SiO₂ slag prevents dissolving of large amounts of lime, and FeO is a necessary factor to dissolve lime. The three factors needed to dissolve large quantities of lime are FeO, temperature and time of contact. By preventing the dissolving of lime and retaining our fluid slag, FeO does not build up in the slag. In addition to preventing

FeO from building up in the slag, a low lime charge materially speeds up the furnace operation by allowing the heat to melt faster, and extra lime can always be added if needed in the later stages of the heat.

L. F. REINARTZ,* Middletown, Ohio.—What do you do when the heat melts with high iron oxide?

W. J. REAGAN.—As a rule, we cannot do anything. That is, the idea is to keep the FeO low and build it up to the desired amount in the final slag. As mentioned in the paper, it is probably possible to reduce iron oxide with a silicon addition, either in the form of 50 per cent silicon or sand, but at this time we do not have enough data to give any information along that field. Possibly Dr. Herty might know where that is being done. The very idea of the iron-oxide control is to keep the oxide low and add what is needed to bring it up to the final figure that is necessary to control the phosphorus.

L. F. REINARTZ.—Dr. Herty, have you had any success in reducing iron oxide in high-carbon steel?

C. H. HERTY, JR.,† Pittsburgh, Pa.—Before I answer that question, I would like to answer a point that Mr. Carlin brought up. When you try to talk about high silicon and low iron oxide, and why one is high and the other low, you are apt to get into a circle, where one effect follows another, and I think very often we get mixed up as to what is the cause and what the effect.

In the work we did at Edgewater, we used our new viscosimeter to measure the fluidity of the slags. We took many measurements with it. We had a complete record of that. It was apparent from the start that the real reason for low iron oxide with high silica was because there was an extremely fluid slag all the way through the heat. With high lime, the slag tended to be very viscous and the transfer of iron oxide from gas to slag was faster than from slag to metal. Therefore, the iron oxide built up. For that particular period of heat we were able to plot the rate at which iron oxide built up against the slag viscosity. We found that after we obtained what normally is called a medium slag, a measurement of about 2 in. on our viscosimeter, all the pick-ups were of about the same nature, they varied only about 10 per cent, but as soon as we had a very heavy slag the pick-up increased and there would be possibly four or five times the rate of build-up of iron oxide in a heavy slag than in a fluid slag. That is particularly true during the lime boil when there are lumps of lime dissolving in the slag, making the bottom of the slag so stiff that at times samples could not be taken. We concluded that it was not the basicity of the slag in this period because the slags are all on the acid side when melting down, but it was the viscosity.

So if the slag was kept thin by the use of high-silicon iron, the tendency was to prevent iron oxide from building up and the heat naturally came low in FeO. On the other hand, if an iron low in silicon was charged the heat finished high in iron oxide. That was checked out on every heat that we followed, about 25 or 30.

When the period after the heat is melted is reached and working is begun, it becomes very apparent that in that case the basicity in addition to fluidity affects the iron oxide very much, and if the percentages of silica and lime are tabulated it will be found that above a certain range of values in the high-lime side there will be a pick-up of iron oxide in the slag. On the other hand if the lime and silica are below

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† Director of Research, Mining and Metallurgical Advisory Boards to the Carnegie Institute of Technology.

certain critical values there will be a definite loss of iron oxide from the slag and at some intermediate range the slag will stay almost constant in iron oxide.

The thing we are interested in is why that happened, because if we know why, we can do something about it. There are certain objections to our method of measuring fluidity with respect to the melting points of slags. The normal time taken to pour a sample for slag viscosity is 3 to 4 sec. after the spoon is taken out of the slag. On siliceous slags the spoon may be held above the viscosimeter for a minute to a minute and a half with very little loss in fluidity, but with basic slags there is an immediate loss of fluidity if the spoon is held longer than 4 sec. In other words, siliceous slags have very slight change in viscosity with falling temperature. If there is a temperature gradient in the slag, as there must be when the metal is being heated, you can see that in a basic slag the bottom of the slag must be less fluid than the top, whereas acid slags would have the same fluidity all the way through. The difference between these fluidities will mean a great difference in rates of transfer from the gas into the slag and from the slag into the metal. On that basis, there is absolutely no reason, if there is high iron oxide in the slag, why you should not add sand to stop the iron oxide from building up, or actually to get a decrease. I know of one company that does that constantly.

We find that the same methods of control we used on this high-carbon killed steel apply to rimmed steel, except, of course, that in the latter an entirely different iron oxide content is desired.

R. C. GOON,* Pittsburgh, Pa.—If we combine the conclusions in this paper with the conclusions in papers that have appeared in the last few years in regard to iron oxide in slag and iron oxide in steel, we are led to believe that a high-phosphorus steel would be a clean steel. Did Mr. Reagan find that to be the case in any of his work, between, say, two steels, one of 0.025 per cent phosphorus and one of 0.012 per cent phosphorus? Is there a difference in the quantity of inclusions?

W. J. REAGAN.—I am unable to answer that question directly, but I know that at one of the Pittsburgh plants the steels higher in phosphorus are considered the cleaner steels. Perhaps a little later on in the investigation we have under way we can tell more about it. In the lower carbon steels, that is very typical.

C. H. HERTY, JR.—We have recently had six heats of low FeO and six of high FeO, picked for their FeO content alone, and compared them by inclusion count for cleanliness. In the tapping slag on the six heats of low FeO steel we get an average of about 0.010 per cent inclusion by the inclusion count and on the high FeO slags, the average was 0.018. The high FeO slag gave steel just about twice as dirty as the low FeO slag. The ingot size was the same in all tests.

L. F. REINARTZ.—The heat containing low FeO produces a steel with relatively high phosphorus, and that is the cleaner steel. You would not attempt to go down to 3 or 4 per cent FeO in the slag of a high-carbon heat, would you?

W. J. REAGAN.—No. We are rather on the edge just now. We are trying to choose the iron oxide we should try for. Apparently phosphorus around 0.025 per cent is much more to our advantage, as far as clean steel is concerned, than a lower phosphorus. Just at present we are not sure just what we want, but it seems to be in that neighborhood.

L. F. REINARTZ.—Furthermore, in plants where various grades of steel are being made instead of one grade of high-carbon steel, it is much more difficult to reach

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extremely low iron oxide content in the slags, as Mr. Reagan has reported. In our practice we cannot reduce the iron oxide as low as reported because our furnace banks are more or less polluted with iron oxide from rimming steels. It is, therefore, very difficult to obtain very low iron oxides in the slag.

H. W. GRAHAM,* Pittsburgh, Pa.—I wonder if we should not be a little cautious in our thinking about phosphorus content. Let us not make the mistake of thinking that we can afford to greatly increase the phosphorus content for the sake of an apparent increase in cleanliness. After all, we are not running an open hearth just for pleasure. We are trying to make a product that is useful to the user of the steel, and on that basis I would be very careful about the level selected for phosphorus content. We know perhaps less about what phosphorus really does to steel than almost anything else in the whole steel business; and the effect upon the physical properties of the resulting steel and its behavior through the many operations that steel is subject to is something that should be borne in mind. That may not be true between relatively minor variations of phosphorus content. I would not suppose that it would be true between a phosphorus of perhaps 0.008 and 0.018, but if the phosphorus content does vary widely I would expect to find some kind of an answer, and perhaps an unfavorable one, in steel quality.

W. J. REAGAN.—I did not intend to say that we would increase the phosphorus beyond our present limits, which are 0.04 per cent. The idea I wished to present is that we can control the phosphorus very accurately in the final steel analysis. If we find 0.010 per cent desirable we can finish the steel within a very narrow range of this figure. If we find 0.020 phosphorus more desirable, we can easily finish the heats within a very narrow range of 0.020 phosphorus.

MEMBER.—In steels containing in the neighborhood of 0.01 per cent phosphorus, has there been identified in the inclusion count of these steels any phosphorus?

C. H. HERTY, JR.—We did some work three years ago to see how much phosphorus there was in electrolytic residue and it was so small that it was questionable whether there really was very much there. That was on steel of about 0.020 or 0.025 per cent phosphorus. In other words, we got just a trace of phosphorus; not nearly as much as of sulfur.

* General Metallurgist, Jones & Laughlin Steel Corporation.

Critical Studies of a Modified Ledebur Method for Determination of Oxygen in Steel, II

By T. E. Brower,* B. M. Larsen* and W. E. Shenk,* Kearny, N. J.

(New York Meeting, February, 1934)

SHORTLY after our previous paper on this subject was printed,¹ we located a source of uncertainty in the results arising from the unexpected fact that hydrogen slowly reduces silica at 1100° C. in presence of iron, even when the iron nowhere touches the silica, although in absence of iron it does not do so. This difficulty has been completely obviated by the use of a small high-frequency furnace, which enables us to heat the specimen for analysis without raising the temperature of the silica vessel to a point at which any appreciable reduction of the silica glass occurs. We now describe this modification of procedure, and present some typical results obtained with it. For any given specimen of steel, the results are entirely definite and reproducible, but their precise significance is still open to some question, as indeed is true of all methods of oxygen determination so far developed. Further elucidation of this question is to be expected from the cooperative comparison of the several methods now under way under the auspices of the Bureau of Standards at the instance of the Iron and Steel Division of the A.I.M.E.

APPARATUS

The final form of apparatus we have used is identical with that described and illustrated in our previous paper, except for the substitution for the Globar furnace of a small high-frequency furnace actuated by a vacuum tube oscillator² of about 1.5 kw. capacity, and for a slight modification of the containing vessel. This transparent silica vessel is illustrated in Fig. 1 of this paper. Its enlarged portion is about 5 cm. in diameter and 13 cm. long. The silica tube for inlet of hydrogen is fused into this bulb and ends beneath the metal "bucket" holding the steel sample. This sample is in the form of fine millings. The "bucket" is suspended by a platinum wire from the cap of Pyrex glass. The high-frequency

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¹ B. M. Larsen and T. E. Brower: Critical Studies of a Modified Ledebur Method for Determination of Oxygen in Steel. *Trans. A.I.M.E.* (1932) 100, 196-227.

² General Electric Co. tube converter, as per specifications RA-1322, supplied by Ajax Electrothermic Corporation.

coil, which comprises 14 turns of water-cooled copper tubing, is 5.5 cm. diameter and 10 cm. long; it is arranged so that it may readily be raised about, or lowered away from, the silica vessel.

Temperature is measured by an optical pyrometer sighted down into the bucket through a small silica window sealed into the Pyrex cap.

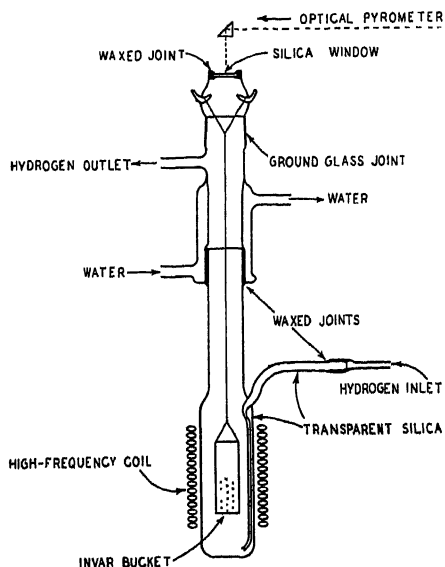


FIG. 1.—SILICA VESSEL AS USED WITH INDUCTIVE HEATING OF THE SAMPLE.

The readings were calibrated by observing the melting of a small piece of pure copper placed on top of the sample.

Container for Sample.—This bucket is really the heating unit, for the current induced in it sets up a magnetic field, which lessens the field inside the bucket to such an extent that little heat would be developed within the sample even if it were a solid piece of metal. That the sample is finely divided tends to aggravate this condition because the effective electrical resistance to the induced current is high as compared to that of a single block of the same metal. Selection of the test material for the bucket consequently is based largely upon electromagnetic

requirements; namely, that it should be as nonmagnetic as possible at room temperature, that its magnetic transformation, if any, should occur at a relatively low temperature, and that its specific resistance should be relatively high. It should be nonmagnetic because the tuning of the oscillator for satisfactory operation depends upon the magnetic characteristics of the bucket; if the tuning is proper for the nonmagnetic condition, which is that of any bucket at the final temperature, it will not be right at low temperature for a bucket which is then magnetic. Moreover, if the change in magnetic characteristics is large and occurs at a high temperature, one would have to adjust the tuning with care in order to utilize the power effectively, for otherwise much of the power delivered to the oscillator appears as heat in the plates of the tubes, which may thus be damaged.

After some trials with iron, nichrome, and stainless steel, we finally used a bucket of Invar (35 per cent nickel, 65 per cent iron), which has a relatively high electrical resistance and ceases to be appreciably magnetic at relatively low temperature. The bucket finally used, machined out of a solid rod of Invar, is 2.2 cm. diameter, 6.5 cm. long, and about 0.5 mm.

wall thickness. A number of very small holes were pricked in the lower portion of the bucket to facilitate the circulation of hydrogen through the sample of millings. Such a bucket apparently can be used indefinitely.

In order to remove all oxygen from the metal of a new bucket, it was heated in hydrogen at 1200° to 1250° C. for 6 to 8 hr. With a bucket so treated, we have repeatedly obtained blank values of 0.1 mg. H_2O , or less, for periods of heating of 2 to 3 hr. This constitutes a real check on the method because such a blank reproduces all the conditions of the actual determination; and shows that with inductive heating, such that only the sample and the oxygen-free bucket are at the high temperature, we have removed the last source of blank error.

Overload Relay for Oscillator Circuit.—In order to obviate damage to the tubes in case the oscillations are suppressed for any reason, it was considered advisable to provide for an automatic shutoff of the plate voltage in that event. The manufacturer states that the maximum safe power dissipation at the plates is that which heats them to a "cherry red," about 800° C. If the power dissipated at the plates of the tubes exceeds this value, the protective device must interrupt the plate supply at once. To accomplish this a modification of a scheme used by Adcock³ was used. Since it is not practical to obtain a direct measure of the power absorbed in the plates as a means of motivating the protective device, indirect measurement is made. The power absorbed in the plates is the difference between the total power supplied to the plate circuit from the plate transformer and the power absorbed in the furnace coil and its charge. For any fixed given condition of charge and plate voltage, the input power is proportional to the plate current, and the power absorbed in the furnace is proportional to the voltage across the terminals of the furnace coil. If then the plate current, or a small portion of it, is allowed to flow through one coil of a differential relay, and the furnace terminal voltage is rectified and the resulting d.c. voltage applied to the other coil of the relay, the relay can be made to trip at any desired plate condition by adjustment of the current in the relay coils. Instead of using the terminal voltage at the furnace coil, suitably reduced by means of a voltage divider (as used by Adcock), it was considered somewhat safer to place a small, one-turn secondary coil on top of the furnace coil, but well insulated from it, to supply a voltage proportional to the furnace voltage. This voltage was rectified and applied to the relay coil through suitable resistances. The differential relay was a Model 30 Weston galvanometer relay, which was specially wound for this application. The rectifier, of the copper-copper oxide type, was built into the relay case. Since the contacts of this relay were not heavy enough to break.

³ F. Adcock: A Valve-operated Coreless Induction Furnace for High-temperature Research. *Trans. Faraday Soc.* (1930) 26, 544-560.

the primary current of the plate transformer directly, a second relay capable of breaking 15 amp. was operated by the first to open the plate transformer circuit. The arrangement of the protective circuit in relation to the main oscillatory circuit is shown in simplified form in Fig. 2.

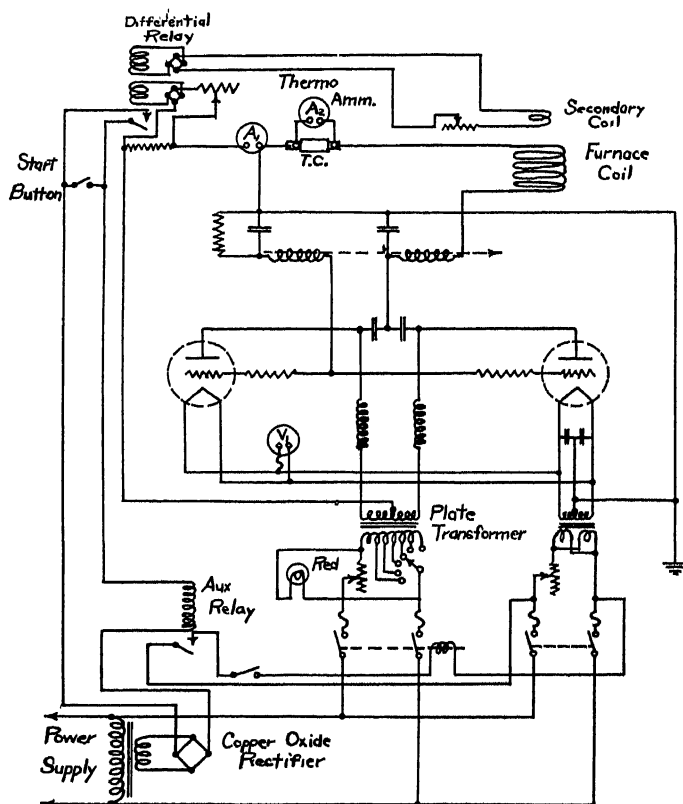


FIG. 2.—WIRING DIAGRAM OF HIGH-FREQUENCY GENERATOR WITH PROTECTIVE CIRCUIT AGAINST OVERLOAD.

GENERAL MODE OF OPERATION

A sample of millings of the steel is put in the bucket, which is then suspended in the containing vessel (Fig. 1); purified hydrogen is passed through, escaping at the stopcock between the silica bulb and the first absorption tube. A small electric resistance furnace is now raised about the bulb so that bulb, bucket and samples are all heated to 530° to 550° C. and maintained there for 80 to 100 min.; this suffices to remove all surface oxygen from the sample as well as any oxygen-containing gases that may have been absorbed on the walls of the bulb. The weighed absorption tubes are now connected, and the hydrogen stream passed through the whole train;

the furnace is removed and replaced by the high-frequency coil, and the temperature inside the bucket is raised to 1120° to 1150° C. and maintained within these limits, as can readily be done by occasional observation and adjustment in spite of minor variations of line voltage. Under these conditions the oxygen is substantially all removed in 100 to 120 min., and appears as H_2O in the two absorption tubes, which are finally weighed again.

There is some volatilization of metal from bucket and sample, at 1150° C. in a hydrogen atmosphere, though much less than there would be in a vacuum. This results in the gradual formation of a black film over the inside surfaces of the silica bulb. We have made a practice of removing this metal film by soaking the bulb in acid after every dozen determinations, but we have never seen any indication that this film causes any blank error, presumably because the silica walls, heated during the actual determination only by radiation from the bucket, are not at a temperature above 400° C. Occasionally we have had a blank correction of 0.2 to 0.3 mg. H_2O per hour arising from an incompletely reduced catalyst; but normally the blank correction is now practically zero.

Separation of Surface Oxygen from Oxygen Contained in the Metal.—The question has been raised as to whether in the pretreatment of the sample in hydrogen at 500° to 550° C. for 100 min. we succeed in removing *all* of the surface oxygen but *none* of that contained in the steel. It is almost impossible to answer this question definitively. We have only indirect evidence, which points unmistakably, in our view, to the substantial reliability of our procedure. On the one hand, the curve of oxygen evolution at this low temperature flattens out definitely within this period, no weighable amount of water being evolved after 2 hr. additional. Moreover, analysis of a sample of a 0.5 per cent aluminum-iron alloy gave less than 0.1 mg. H_2O in both absorption tubes together, and an ingot-iron sheet, previously treated in moist hydrogen at 1500° C. for 18 to 20 hr., yielded only 0.002 per cent oxygen. These low values show that the amount of surface oxygen not removed by the low-temperature treatment must be almost negligible, of the order of 0.001 per cent or less. On the other hand, that this pretreatment does not remove any appreciable amount of the dissolved oxygen is probable from (1) the low diffusion rate of oxygen in steel even at 1100° C. (discussed in a later paragraph), a rate which must fall to an extremely low value at 550° C., and (2) the fact that in several cases our value for oxygen content is somewhat higher than the value obtained by the vacuum fusion method on the identical material in massive form.

Absorption of Nitrogen Evolved from Sample.—The comparison just alluded to brings up the question whether our slightly higher results could be attributed to the absorption of some form of nitrogen evolved from the sample. At 1100° C. NH_3 and most of the other possible

nitrogen compounds should be almost completely dissociated, but it is not certain that the gases leaving the sample will be at the equilibrium corresponding to the temperature of the sample. To check this possible source of error, the total combined nitrogen content of the P_2O_5 in each absorption tube was determined, after the tubes had been used for the analysis of 30 to 40 steel samples; this was done twice. In both cases the first tube contained about 2 mg. of nitrogen and the second tube contained none. By totaling up the nitrogen content of all the samples that had been run in each series, it was found that the amount

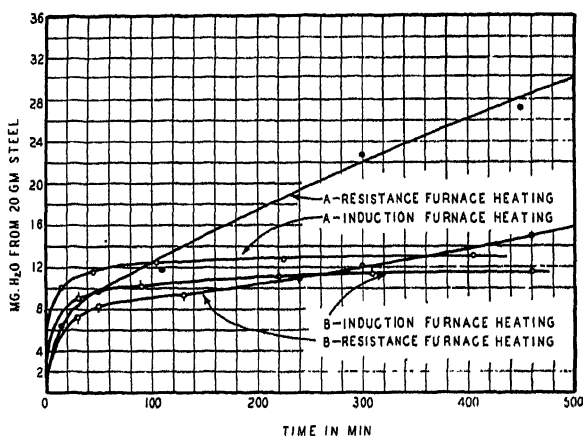


FIG. 3.—OXYGEN-EXTRACTION CURVES (A) FOR 0.9 CARBON, (B) 0.09 CARBON STEEL, WITH BOTH RESISTANCE (AT 1120° C.) AND INDUCTIVE HEATING (1150° C.)

of nitrogen in the absorption tube amounted to from 10 to 15 per cent of the nitrogen contained in the samples used. The nitrogen content of all ordinary steels runs between 0.002 and 0.018 per cent, so that this source of error would in no case be more than the equivalent of 0.002 per cent oxygen. Although an approximate correction can be made on this basis (around 0.001 per cent or less for basic open-hearth steel and 0.001 to 0.002 per cent for electric or bessemer steel) it is almost too small to be of any significance, since the probable error in the whole procedure is about ± 0.002 per cent oxygen. It is probable that this small amount of combined nitrogen from the sample is in the form of ammonia. Nitrogen atoms on the surface of the sample may have a tendency to evaporate as NH_3 molecules, and all of these may not break down to nitrogen and hydrogen before they are carried out of the heated zone in the bulb.

Rate of Extraction of Oxygen.—This is illustrated by Figs. 3 and 4. In the former the curves represent the actual cumulative weight of H_2O recovered on successive heating periods from two steel samples, both with the resistance heating through the bulb as used previously and with inductive heating of the sample. Both samples were from the same steel

(a semi-killed bessemer steel with 0.09 per cent C.) but sample A was milled from the outside layer of a bar after pack-carburizing and contained about 0.9 per cent C., whereas sample B was the original uncarburized steel. This comparison brings out clearly the larger blank error of the previous method, particularly with higher carbon steels, and the practical elimination of this error with inductive heating. The more rapid initial extraction of oxygen with the newer set-up is presumably due to the higher temperature, 1150° as compared to 1120° C.

In Fig. 4, curve A is for a 30-gram sample of ingot iron, this sample being the so-called "international sample" from the Bureau of Standards

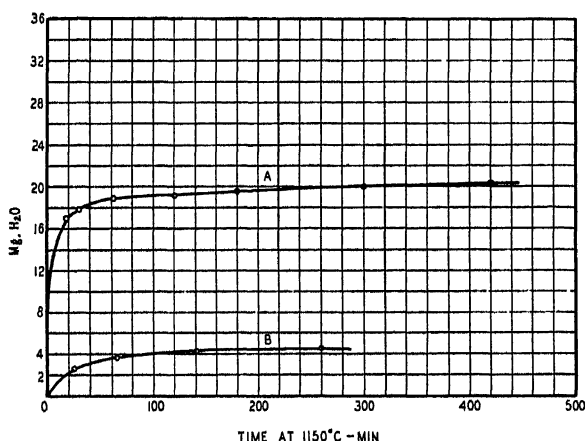


FIG. 4.—OXYGEN-EXTRACTION CURVES FOR (A) 30 GRAMS INGOT IRON; (B) 20 GRAMS ELECTROLYTIC IRON.

in which the oxygen had been determined, both there and at Aachen, by the vacuum fusion method, according to which the oxygen content⁴ was 0.055 to 0.062 per cent. Curve B is for a sample of electrolytic iron. On the basis of these, and of a number of other similar curves, we have chosen a period of 110 to 120 min. for ordinary samples; for after this period the curve is either entirely flat or rises very slowly. Using this period we get definite and quite reproducible values; thus for the ingot iron (curve A) 0.057 per cent and for the electrolytic iron (curve B) 0.018 per cent oxygen.

DIFFUSION RATE OF OXYGEN THROUGH STEEL AT 1100° C.

The data in Figs. 5 and 6 are included here chiefly because they show that the mechanism of oxygen extraction from a sample of solid steel

⁴ H. C. Vacher and L. Jordan: Determination of Oxygen and Nitrogen in Steels by the Vacuum-fusion Method, U. S. Bur. Stds. *Jnl. of Research* (1931) 7, 375-401.

is probably a true diffusion process. The curves in Fig. 5 show the rate of oxygen evolution at 1100° C. (as milligrams of water vapor from 20-gram samples) from a sample of bessemer steel with an "oxygen content" of about 0.045 per cent. The material, instead of being fine millings,

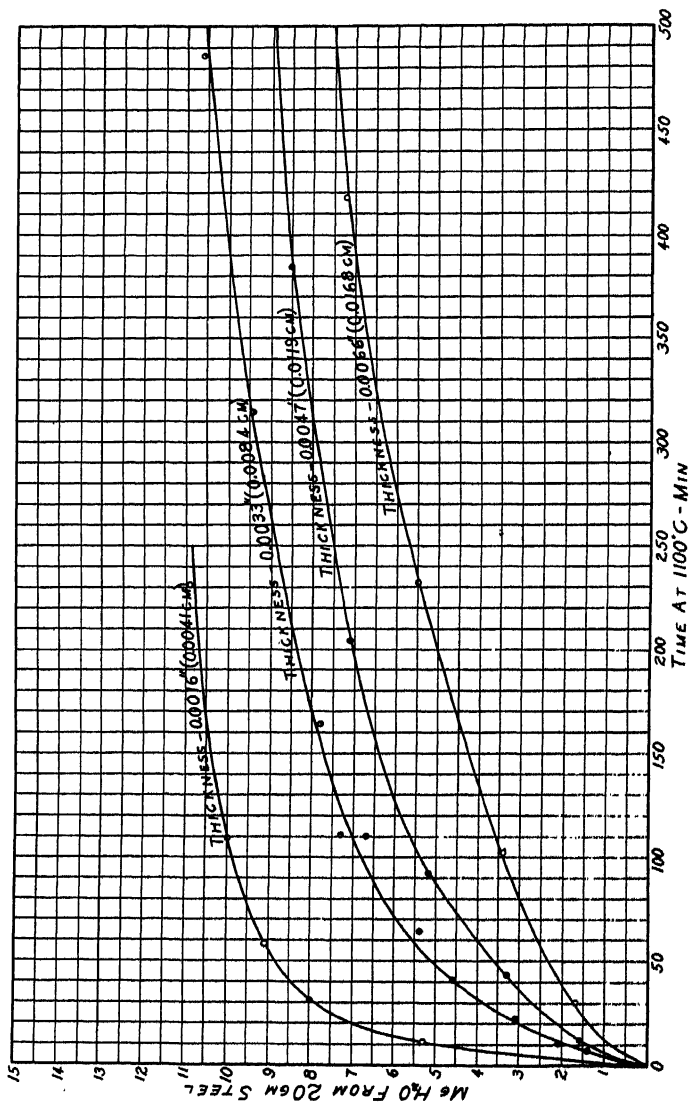


FIG. 5.—OXYGEN-EXTRACTION CURVES FOR 20-GRAM SAMPLES OF THE SAME STEEL IN THE FORM OF THIN RIBBON OF DIFFERENT THICKNESSES.

was in the form of very thin ribbon, crumpled up and packed into the metal container; the only variable between the curves in Fig. 5 is the thickness of the ribbon, the values being 0.0066, 0.0047, 0.0033 and 0.0016 in. for the four samples, all from the same steel. This gives a definite

distance for diffusion before the oxygen atoms reach the surface of the metal, and the process can then be treated mathematically on the basis of the postulates that: (1) the law of diffusion is applicable, (2) the initial concentration of oxygen in solution through the ribbon sample is uniform, and (3) oxygen atoms diffuse through the solid metal to the surface

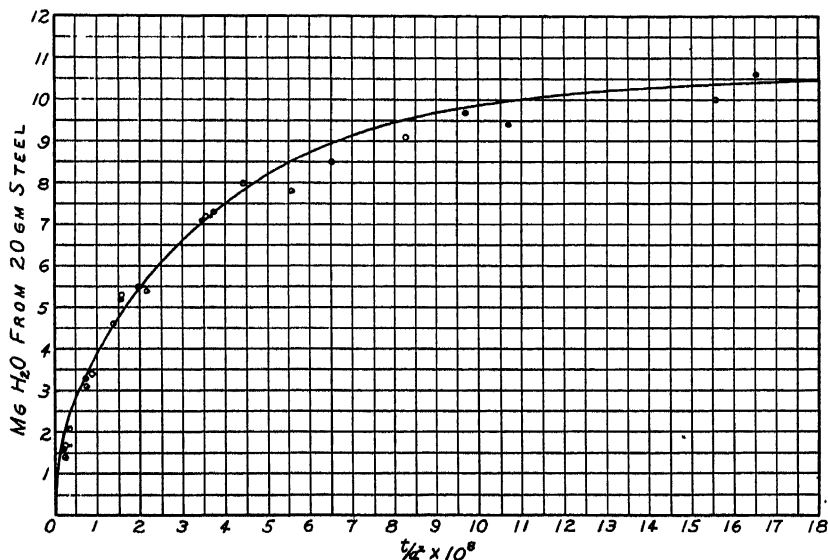


FIG. 6.—OXYGEN-EXTRACTION DATA OF FIG. 5 PLOTTED AGAINST t/a^2 AND COMPARED WITH THE CURVE OF EQUATION 2 ($k = 1.08 \times 10^{-9}$).

whence they evaporate very quickly as H₂O molecules. Solving the usual differential equation representing Fick's law

$$\frac{\partial c}{\partial t} = k \frac{\partial^2 c}{\partial x^2} \quad [1]$$

for the boundary conditions present here—that is, for a thin plate exposed on both sides—we get the following series:

$$Q = 1 - \frac{8}{\pi^2} \left(e^{-\frac{kt}{a^2} \cdot \frac{\pi^2}{4}} + \frac{1}{3^2} e^{-\frac{kt}{a^2} \cdot \frac{3^2 \pi^2}{4}} + \frac{1}{5^2} e^{-\frac{kt}{a^2} \cdot \frac{5^2 \pi^2}{4}} + \right) \quad [2]$$

where c is oxygen concentration at the distance x from the plate surface, Q is the fractional amount of the total oxygen diffusing to the surface in time t , k is the diffusivity constant and $2a$ is the thickness of the plate.

This is a rapidly converging series, so that even the second term is very small except for small time periods. Inspection of formula 2 shows that if the factor kt/a^2 , which is common to all the exponents, is held constant, Q must remain constant. This condition is fulfilled if the square of the thickness a is increased proportionally with the elapsed

time or with the coefficient of diffusion k . This conclusion is important in comparing the experimental results obtained with specimens of different thickness; since, if k remains constant, and the time scale is changed proportionally to the square of the thickness of each specimen, the curves obtained will be identical. This is done in Fig. 6, in which oxygen evolved as H_2O was plotted against t/a^2 , and it is clear that all the points fall very close to a single curve, in accordance with the formula. The curve drawn in Fig. 6 is the curve of equation 2 for $k = 1.08 \times 10^{-9}$, the value averaged from those given by the several experimental values. The close agreement between the experimental points and the theoretical curve for diffusion suggests that this value of k is reasonably reliable; but it would be desirable to check it on a series of pure iron-oxygen alloys. There is no reliable figure for the solid solubility of oxygen in steel at $1100^\circ C.$, and so we cannot be sure that the second postulate above is strictly fulfilled.

This result points strongly to the conclusion that we are dealing here with diffusion of oxygen through the solid metal, on which basis the value of k represents the specific diffusivity of oxygen through steel at $1100^\circ C.$ This value is very much lower than those reported by Bramley⁵ for carbon and nitrogen at the same temperature, namely:

	k AT $1100^\circ C.$, SQ. CM. PER SEC
Carbon.....	45. $\times 10^{-8}$
Nitrogen.....	40. $\times 10^{-8}$
Oxygen.....	0.1 $\times 10^{-8}$

This comparison indicates that oxygen diffuses much more slowly than carbon. This is in harmony with the experience of Decroly,⁶ who was unable to detect any appreciable diffusion of CO through a thin steel tube at $1000^\circ C.$ It is very probable that CO molecules cannot diffuse as such through solid steel; yet, if oxygen could diffuse at a rate comparable with carbon, one would expect that an appreciable number of oxygen atoms produced by dissociation of CO could diffuse through the metal, and then recombine with carbon to reform CO on the other side.

RATE OF EXTRACTION OF VARIOUS OXIDES BY HYDROGEN FROM STEEL AT $1100^\circ C.$

So far we have considered the oxygen as if it were all dissolved in the steel; but oxygen occurs there in other forms also, and it is important to ascertain, if possible, which of these several varieties are recovered in any

⁵ A. Bramley: The Diffusion of Carbon and Nitrogen into Iron and Steel. Iron and Steel Inst., *Carnegie Schol. Mem.* (1926) 15, Pt. 2, 155-74.

The dimensions of k are $cm.^2/sec.$; the numerical value applies when time is expressed in seconds and the thickness of metal in centimeters.

⁶ C. Decroly: Study of the Diffusion of CO through Steel in the Neighborhood of 800° and $1000^\circ C.$ *Chim. et Ind. Special No. 484-9* (March, 1931).

method of extraction and analysis. For the present discussion, we may classify the possible forms as: (1) FeO oxygen, which may be present either as (a) oxygen atoms "dissolved" or dispersed through the lattice of the iron, or (b) FeO inclusions, precipitated in the liquid iron or during freezing, and perhaps also as tiny particles separated from solid solution; or (c) FeO present as a constituent of oxide or silicate inclusions; (2) MnO, SiO₂, Al₂O₃, or other oxides present in inclusions.

Through the courtesy of Dr. C. H. Herty, Jr., we had available several specimens of steel that had been made by treating small samples from the same bath of steel with different deoxidizers so that each sample should contain substantially only a single type of inclusion. The composition of four of these samples is shown in Table 1.

TABLE 1.—*Composition of Samples Containing Definite Types of Inclusions*

Sample	C, Per Cent	Mn, Per Cent	Si, Per Cent	Deoxidizer
A	0.04	0.08	0.008	None
B	0.07	0.10	0.003	Aluminum
C	0.07	0.11	0.185	Silicon
D	0.07	0.65	0.008	Manganese

The rate of extraction of oxygen from these four samples is shown in Fig. 7. In A, which was poured wild, some of the oxygen present in the liquid metal had escaped as CO gas during the freezing of the ingot, but

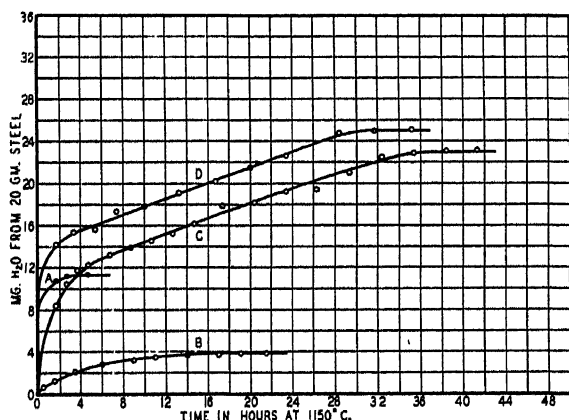


FIG. 7.—OXYGEN-EXTRACTION CURVES FOR SAMPLES FROM A SINGLE EXPERIMENTAL HEAT: (A) NOT DEOXIDIZED; (B) KILLED WITH ALUMINUM; (C) KILLED WITH SILICON; (D) KILLED WITH MANGANESE.

that remaining was un doubtedly present essentially as FeO inclusions and dissolved oxygen: its curve flattens out almost completely after a little over 2 hr. at 1150° C. Nearly all the oxygen in B should be present as

Al_2O_3 inclusions, which may contain a small percentage of FeO , with a very small amount of dissolved oxygen; its curve finally flattens at a value for oxygen which is only a fraction of that present as Al_2O_3 . The first 1 to 2 mg. H_2O may represent dissolved oxygen, but the extra 2 mg. must have come either from FeO contained in the Al_2O_3 inclusions or possibly from a slow reduction of the very tiniest Al_2O_3 particles. From C, deoxidized with silicon, we obtained during the first $1\frac{1}{2}$ to 2 hr. a rapid extraction of what is presumably dissolved oxygen together with FeO in inclusions; the curve then gradually rounds off until after about 4 hr. it settles down to a steady rate of about 0.35 mg. H_2O per hour, which almost certainly represents a slow reduction of SiO_2 inclusions. This continues up to about 36 hr., after which the curve flattens off definitely, indicating complete recovery of all oxygen in the sample. In our earlier paper evidence was given that SiO_2 does reduce slowly in hydrogen, *when either platinum or iron is present*, and there is little reason to doubt that this happened with the SiO_2 inclusions in the present case. With D, deoxidized with manganese, the curve is very similar, settling down after 2 to 3 hr. to a slow rate of reduction of MnO , this rate being almost exactly the same as that for SiO_2 .

In general, these results indicate that in the 2-hr. period of heating used in the analyses we should obtain essentially all the oxygen present as dissolved oxygen or FeO inclusions and probably a large part of the FeO present in inclusions of silicates or oxide mixtures, but only negligible amounts of the oxygen present as SiO_2 , MnO , and Al_2O_3 . In any case, obviously the amount of oxygen extracted in a given period from inclusions will depend not only upon their amount but also upon their size and distribution; and this circumstance makes us wonder whether any *absolutely* clear-cut separation of the several forms of oxygen is feasible by any single method. In a recent paper on vacuum fusion extraction, Reeve⁷ describes a method for substantially separating the fractions of the total oxygen present as FeO , MnO , SiO_2 and Al_2O_3 by successive heating periods of 1000° to 1050° C., 1150° C., 1300° C., and 1550° to 1600° C., respectively. Our results are in general accord with his, in so far as comparison is possible, except that in the present work the reduction rates for MnO and SiO_2 at 1150° in the solid metal in hydrogen seem to be very nearly the same. Reeve's results indicate that (in his set-up with the steel melted into a tin-iron alloy) the SiO_2 requires a higher temperature for rapid reduction than MnO .

In a recent paper, Chipman⁸ gives some calculated curves for equilibrium between silicon, manganese, aluminum and the residual FeO in the

⁷ L. Reeve: Improvements in the Vacuum Fusion Method for Determination of Gases in Metals. This volume p. 82.

⁸ J. Chipman: Application of Thermodynamics to the Deoxidation of Liquid Steel. Amer. Soc. Steel Treat. Preprint 18 (1933).

liquid steel. The values in Table 2, estimated approximately from his curves, are compared with the values for about 100 min. of heating from Fig. 6. These values do not check particularly well, especially for the silicon deoxidation, but they are in the same order and at least tend to substantiate Chipman's conclusion that aluminum is a much stronger deoxidizer than silicon.

TABLE 2.—*Estimated Values from Chipman's Curves*

Sample	Per Cent Oxygen by H ₂ Reduction	Per Cent Oxygen in Liquid Steel, Calculated	Deoxidizer
B	0.005	0.0005	Aluminum
C	0.035	0.008	Silicon
D	0.062	0.08	Manganese

Of the four "varieties" of oxygen in steel listed above, we believe that this modified H₂ reduction method gives us: forms 1a and 1b (dissolved oxygen and FeO inclusions) with fair completeness, but only a negligible amount of form 2 (oxygen from MnO, SiO₂ and Al₂O₃). The real difficulty with the interpretation of oxygen values by this method arises from the fact that it very probably gives also most of the oxygen of variety 1c; i. e., that present as FeO contained in oxide or silicate inclusions, where the FeO is mixed with MnO and SiO₂, which are formed by precipitation in the liquid metal and during freezing. In such cases, the amount of oxygen remaining in solid solution in the steel at the freezing point just after solidification is complete will depend only on the *composition* of the inclusions (increasing with their FeO content) and not at all upon the *amount* of these inclusions. This means that some caution must be used in interpreting the oxygen values obtained by H₂ reduction, or for that matter, by any other method. The interpretation is aided by determining the amount and composition of the inclusions by microscopic examination or by some inclusions extraction method, and by a knowledge of the details of the deoxidation procedure employed in making the steel. For example, we found an oxygen content of only 0.014 per cent in the rim portion of a rimmed basic open-hearth ingot; this steel was very clean, but the few small inclusions were rich in FeO and nearly all the oxygen found was probably solid solution oxygen. In bessemer steel completely killed with an excess of silicon-zirconium alloy, we found only 0.007 per cent oxygen, but this steel was extremely dirty, and there was probably almost no solid solution oxygen, the small amount recovered being largely present as FeO in the large amount of zirconium silicate inclusions present. In a semi-killed bessemer steel, on the other hand, the H₂ reduction analysis gave 0.038 per cent oxygen, a large part of which was present as FeO in the large amount of ferrous silicate inclusions contained in this very dirty steel.

TYPICAL RESULTS ON VARIOUS STEEL AND IRON SAMPLES BY THE H_2 REDUCTION METHOD AT $1150^\circ C$.

Table 3 lists values for oxygen by the H_2 reduction method in different types of samples. In some cases, several samples of one type were analyzed; in a few cases, only one sample is represented.

TABLE 3.—*Typical Oxygen Values by the H_2 Reduction Method*

Sam- ple No.	Description of Sample	"FeO Oxygen" Content, Per Cent O_2
1	Open-hearth ingot iron, C 0.02 per cent, no excess Si or Al	0.040-0.060
2	Electrolytic iron	0.018-0.024
3	Pure iron melted in vacuum	0.003-0.006
4	Ingot-iron sheet treated for 16 to 20 hr. in H_2 at $1500^\circ C$.	0.002
5	Carbonyl iron, pressed from powder and rolled to solid sheet	0.012
6	Iron-aluminum alloy, 0.25 per cent Al	0.002
7	Iron-aluminum alloy, 0.50 per cent Al	0.000 (trace)
8	0.06 to 0.08 per cent C steel poured wild with no deoxidizer	0.049
9	Semi-killed bessemer steel	0.038-0.046
10	Rimmed bessemer steel	0.022
11	Bessemer killed, 0.12 per cent Si, 0.10 per cent Zr	0.007
12	Semi-killed open-hearth steel	0.024-0.030
13	Rimmed open-hearth steel	0.014-0.018
14	Low and medium-carbon killed steels, Si 0.10 to 0.25 per cent, no excess Al used in deoxidation	0.012-0.033
15	Low and medium-carbon killed steel with excess Al used in deoxidation, 0.02 to 0.04 per cent metallic Al	0.004-0.009

Several so-called "pure iron" samples made by vacuum melting with a trace of excess carbon to insure deoxidation have always given a little oxygen, from 0.003 to 0.006 per cent. It is quite possible that all the oxygen in a vacuum melt does not get out of the steel as CO gas, because of a limited diffusion rate from a large mass of liquid metal. Iron reduced in hydrogen at 1400° to $1500^\circ C$. was apparently lower in oxygen, from zero up to 0.002 per cent. The sample listed above (No. 4) was reduced in moist hydrogen; the use of dry hydrogen during the last part of the heating should give a still lower value.

In general, semi-killed steels run higher than rimmed steels, largely because of a greater loss of oxygen as CO gas during freezing of the rimmed steel, and in such semi-killed steels a greater proportion of the oxygen is present as FeO in inclusions. For any one type of steel, bessemer steel is likely to run higher than open-hearth steel. Ordinary low or medium carbon killed steels which have been treated with excess silicon but with little or none of any stronger deoxidizer (such as aluminum or zirconium) do not usually give very low oxygen content by

this method; results have ranged from 0.012 to 0.033 per cent, much of which represents FeO present in the widely variable amount of silicate inclusions always found in such steels. In well made steels of the so-called "nonaging" type, we obtain lower oxygen values, usually around 0.004 to 0.008 per cent; as might be expected from the use of excess aluminum in the ladle, which results also in the presence of 0.02 to 0.05 per cent residual metallic aluminum in the finished metal.

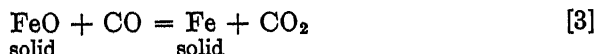
We also made a few comparative determinations of oxygen by this method on the same steel before and after carburizing, with results shown in Table 4.

TABLE 4.—*Comparative Determinations of Oxygen*

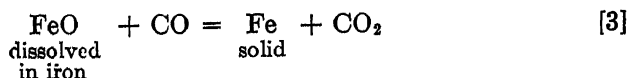
	O ₂ , Per Cent By H ₂ Reduction		
	Original	After Carburization	
Semi-killed bessemer steel	0.043		2-in. square billet, pack-carburized 920° C., 18½ hr. Depth of case 0.10 in. Outer 0.05 in. layer of case. Second 0.05 in. layer of case. Carburized in oxygen-free H ₂ + toluene at 980° C. 27 hr.
		0.049	
		0.043	
		0.032	
Electrolytic iron.	0.022	0.022	Pack-carburized 920° C. 17 hr.
Electrolytic iron.	0.019	0.021	Pack-carburized 920° C. 17 hr.
		0.013	Pack-carburized 1075° C. 17 hr.

Thus there is little, if any, change in oxygen content, as determined by our hydrogen reduction method, during pack-carburization at 920° C.; an appreciable lowering during pack-carburization at 1075° C. and also in the hydrogen-hydrocarbon atmosphere at 980° C. This last lowering would have been much greater undoubtedly but for the slow diffusion rate of oxygen in steel even at that temperature. These results are in harmony with calculations based upon present knowledge of the equilibrium in the reactions concerned.

In the reaction



the solid phases are FeO (containing a little extra oxygen, sometimes called wüstite) and iron saturated with oxygen; if reduction is continued until the FeO phase has disappeared, we have a single solid phase of iron with a varying concentration of FeO, and so write the reaction



the equilibrium constant of which $k_3 = \frac{(\text{CO}_2)}{(\text{CO})[\text{FeO}]}$ where the quantity $[\text{FeO}]$ represents the activity of the dissolved FeO, which becomes unity as soon as the iron becomes saturated with respect to FeO. At 950° C. $k_3 = 0.43$, and therefore

$$[\text{FeO}] = \frac{(\text{CO}_2)}{(\text{CO})} \times \frac{1}{0.43} \quad [4]$$

From Becker's data⁹ on the carburizing equilibrium we find that at 950° C. a gas mixture comprising 14.2 per cent CO_2 and 85.8 per cent CO , or a $(\text{CO}_2)/(\text{CO})$ ratio of 0.165, will just carburize a 0.10 per cent carbon steel. Under these conditions $[\text{FeO}]$ at equilibrium would be, in accordance with equation 4, $0.165/0.43$ or 0.4. The saturation concentration of oxygen in steel at 950° C. is, to take an average of the rather uncertain available experimental results, about 0.05 per cent, this being therefore the concentration at which $[\text{FeO}] = 1$; whence, on the plausible assumption that $[\text{FeO}]$ is proportional to the percentage of this saturation value, the concentration of oxygen in equilibrium at the carburizing conditions specified at 950° C. is 0.05×0.4 or 0.02 per cent. When the steel contains 1 per cent carbon, as in the latter part of the carburizing period, the limiting CO_2/CO ratio at 950° C. is, according to Becker, 0.025, whence $[\text{FeO}] = 0.025/0.43 = 0.05$ and the equilibrium concentration of oxygen $= 0.05 \times 0.05 = 0.003$ per cent. Thus these calculations indicate that there should be little, if any, tendency for oxygen to enter steel while it is being carburized.

On the other hand, determinations of oxygen by the vacuum fusion method published by Grossmann,¹⁰ indicate an appreciable increase in oxygen content during carburization, except on electrolytic iron, where the increase was very small. This apparent discrepancy we attribute largely to the difference in method, as the vacuum-fusion method would show any pick-up of oxygen by manganese, silicon, or aluminum in the steel, whereas the hydrogen reduction would show this, at most, only to a small extent for manganese and silicon and presumably not at all for aluminum. The requisite equilibrium data for these three cases are not sufficiently reliable to justify a thermodynamic calculation; but there can be no doubt that aluminum, and probably silicon, can pick up oxygen even under carburizing conditions provided that oxygen compounds are present in the gas phase in contact with the steel. This view is corroborated by direct evidence, presented by Bain,¹¹ that a 0.5 per cent alu-

⁹ M. L. Becker: Carburizing and Graphitizing Reactions between Fe-C Alloys, CO and CO_2 . *Jnl. Iron and Steel Inst.* (1930) **121**, 337-65.

¹⁰ M. A. Grossmann: Oxygen in Steel. *Trans. Amer. Soc. Steel Treat* (1930) **18**, 600-30.

¹¹ E. C. Bain: Factors Affecting the Inherent Hardenability of Steel. *Trans. Amer. Soc. Steel Treat.* (1932) **20**, 385-428.

minum-iron alloy picked up enough oxygen during pack-carburization to bring about precipitation of particles of alumina in the metal. In any case, we now believe that oxygen plays no essential part in the process of carburization, however it is carried out, although it may exert an indirect influence upon the final result; and we look upon the carburizing process as a diffusion of carbon atoms in solid solution in the metal.

CONCLUSION

Our experience with the modified hydrogen reduction method of oxygen determination described in this paper, which is based upon a large number of results beyond the typical data quoted, leads us to the following conclusions:

1. The surface oxygen on steel samples prepared by milling in air is apparently removed by a preheating of the sample in hydrogen at 550° C. for about 90 min. without affecting the oxygen contained in the steel.

2. The error resulting from slow reduction of silica in the containing vessel is obviated by inductive heating of the sample in a suspended metal bucket which previously has been thoroughly reduced. Under these conditions, and with a properly reduced catalyst for the conversion of CO to H₂O, the blank correction is practically zero.

3. The error arising from the presence of nitrogen in the steel apparently amounts to not more than 10 per cent of the nitrogen present; this is ordinarily a negligible quantity, amounting as a maximum to only 0.002 per cent in certain bessemer steels.

4. Reduction by hydrogen at 1100° C. for 2 hr. apparently extracts: (1) all the oxygen present in solid solution, and (2) substantially all as FeO present in oxide or silicate inclusions. The reduction rates of SiO₂, MnO, Al₂O₃, ZrO₂ are relatively so small as to yield only negligible amounts of oxygen from these sources in a period of 2 hr. The results are entirely reproducible, and we believe them to represent the total oxygen as FeO with an accuracy of 5 to 10 per cent.

5. Oxygen appears to come out of the steel by a diffusion process, since the actual rate of extraction proves to be inversely proportional to the square of the thickness of the metal. The effective specific diffusivity of oxygen in steel at 1100° C. appears to be 0.1×10^{-8} sq. cm. per sec., which is only about one-four-hundredth that of carbon and nitrogen.

SUMMARY OF PROCEDURE NOW IN USE

A representative section (or sections) of the steel sample is cut in air with a milling cutter so as to produce small chips 0.003 to 0.005 in. thick. A 15 to 30-gram sample of these millings is weighed into an Invar bucket previously thoroughly reduced in hydrogen, which is then suspended

inside a silica vessel. Through this vessel is passed, at a rate of 100 to 150 bubbles per minute, a stream of electrolytic hydrogen, freed from all traces of O_2 (by passing over platinized asbestos in a refractory tube at $850^\circ C.$), H_2O and CO_2 . The vessel and sample are heated by means of an external resistance furnace, to 530° to $550^\circ C.$ for a period of 90 to 110 min. (the temperature being checked by a thermocouple adjacent to the bulb within the furnace), the effluent gases passing out into the air through a three-way stopcock; this treatment suffices to remove all surface oxygen from the sample as well as absorbed moisture, etc., from the inside of the silica vessel. This furnace is now replaced by a high-frequency coil, the remainder of the train is connected, and the sample is heated inductively to 1130° to $1160^\circ C.$ (as measured by an optical pyrometer sighted into the bucket) for a period of 110 to 130 min., with a further flushing period of 10 to 15 min. after the sample is cool. The gas stream passes through a sealed Pyrex train, comprising successively: (1) a weighed P_2O_5 tube to absorb H_2O , (2) a double U-tube containing dry $CuSO_4$ on pumice to remove H_2S , (3) a furnace tube containing a thoroughly reduced nickel-thoria catalyst maintained at 260° to $275^\circ C.$, to convert CO_2 and CO to CH_4 and H_2O , (4) a second weighed P_2O_5 tube to absorb the water thus produced, and (5) a bubble tube containing sulfuric acid. The increase in weight of both P_2O_5 tubes, all weighings being against similar counterparts similarly handled, gives the "Fe(Oxygen)" content with an accuracy of ± 0.001 to 0.002 per cent. A single determination requires 4 to 5 hr. The blank correction is not over 0.002 per cent oxygen provided that the train is maintained in good condition, particularly with respect to the catalyst, which should be treated overnight at 320° to $340^\circ C.$ with pure hydrogen every 4 to 6 days. During the final heating the millings sinter together to some extent, but they can be scraped out without injuring the bucket, which is then ready for the next determination.

In preparing the catalyst, we have had the best results by sizing porcelain chips between 5 and 10 mesh, and roughing them by boiling in 1:1 hydrofluoric acid, washing thoroughly and drying; heating 40 grams of the chips so prepared with $Ni(NO_3)_2$ and $Th(NO_3)_4$, in amounts equivalent to 4 grams nickel and 0.4 gram thoria respectively, in sufficient water to cover the chips, stirring constantly until the water is evaporated; and then heating them in a muffle at a temperature not exceeding $350^\circ C.$ until fumes are no longer evolved.

ACKNOWLEDGMENT

The authors are much indebted to Dr. C. H. Herty, Jr., for his courtesy in supplying the group of steel samples deoxidized in various ways.

DISCUSSION

(*L. F. Reinartz presiding*)

L. JORDAN,* Washington, D. C.—It has been suggested that I should take exception to the statement that there might be “something rotten” in the vacuum fusion method. That I am not going to do.

B. M. LARSEN.—I would rather say that we merely have indications of “something rotten” somewhere in one of the methods.

L. JORDAN.—It is a rare analytical method, indeed, that has no shortcomings. One of the difficulties of the vacuum fusion method arises from the coalescence of inclusions; there is a great deal more opportunity for coalescence and growth of the particle size in the vacuum fusion method than in Mr. Larsen's modified Ledebur method. This coalescence cuts down the rate of reduction of inclusions, even though the carbon may be reducing them. One of the advantages of the modified Ledebur method is that such coalescence is not an interfering factor.

MEMBER.—Did you measure the rates of diffusion of oxygen in the vacuum in any of those vacuum-melted samples that were so low in oxygen, and in other impurities as well?

B. M. LARSEN.—I can only answer that in a very qualitative way. We made chips of these vacuum-melted samples, obtaining, of course, a mass of steel chips of varying thickness, but with about the same average thickness as one of these curves. We were able to obtain all of the oxygen in those samples at about the same time as from the ribbon samples, indicating that the rate of diffusion was about the same in the very pure iron.

G. B. WATERHOUSE,† Cambridge, Mass.—I would like to join with Mr. Jordan in thanking the authors for a splendid piece of work. Two things came to my mind that perhaps are not legitimate criticism. In the first place, I thought of Hamilton's paper on the effect of oxygen upon tube piercing (p. 111, this volume). He reached a very clean-cut conclusion. He got good tubes when his oxygen ran on an average of 0.0068 per cent and bad tubes if it ran on an average of 0.010.

Hamilton mentioned high-nitrogen steel. We put a great deal of thought on that a few years ago. F. D. Carney, of the Bethlehem Steel Co., maintained until he died that bessemer steel was not necessarily a high-nitrogen steel. When air is blown through it, it has every chance in the world to pick up nitrogen and should be presumed to be high, but I wonder whether Mr. Larsen has some definite figures comparing bessemer with open-hearth steel.

B. M. LARSEN.—With regard to the nitrogen, I have seen analyses from several sources and we have some of our own. It is almost inevitable that a bessemer steel will run somewhat higher in nitrogen than open-hearth steel. Bessemer steels, as far as I have seen, vary from about 0.010 to 0.020 nitrogen and open-hearth steel from as low as 0.002 to 0.008. The ranges of values in the two types of steel are definitely separated. The fact that the iron in the bessemer converter is in contact with bubbles of air containing initially about $\frac{3}{4}$ atm. of nitrogen pressure makes it almost inevitable that somewhere near a corresponding saturation value for nitrogen under that pressure will tend to be obtained, whereas in the open hearth there is relatively poor contact between metal and gas phases.

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† Professor of Metallurgy, Massachusetts Institute of Technology.

I am much interested in Mr. Hamilton's paper. In a few cases we have been able to obtain correlations between oxygen contents made by our method, and steel properties, chiefly with regard to aging effects. I think that regardless of which is the worst method, in either case relative values can be obtained, and in comparing different steels with regard to one property or another, even if the absolute oxygen content given by the method is not correct, useful information often can be obtained, because they are relatively significant. Mr. Hamilton has been kind enough to supply us with some of his samples, and we are going to try to obtain comparative values.

L. F. REINARTZ,* Middletown, Ohio.—The reported results on rimming steel are so much lower than any figures we ever have, I wonder whether our methods are so inaccurate that we find more oxygen. Why is it that we find at least, I should say, 0.03 to 0.04 per cent oxygen where you show about 0.02 per cent? How many samples did you run?

B. M. LARSEN.—That was an average of three or four different samples, of 0.08 to 0.12 per cent carbon rimmed steel.

S. L. HOYT,† Milwaukee, Wis.—I want to express my appreciation of this work that the authors have been doing. It seems to me that the method has possibilities that have not been fully appreciated.

I have a question to ask relating to manganese oxide and the possibility of its interference in the reduction of iron oxide. The temperature used is 1150° C., and that must be high enough to permit an appreciable reduction of manganese oxide under the conditions of experiment. That suggests that if there is manganese oxide present in the samples, it will be reported in the oxygen content, which the authors appear to be inclined to report as iron oxide. Have they any information bearing directly on this point?

The fractional oxygen determinations carried out by carbon reduction make an attempt to distinguish between iron oxide and manganese oxide, but that distinction is less sharply defined than the distinction between either of those two oxides and silica and alumina. We have become a little more bold on that particular point and now we actually try to distinguish between the iron and the manganese oxide. For the purposes of most metallurgical work, I believe that such a distinction is perfectly logical, only one must bear in mind that the experimental error involved is somewhat larger than is true of silica or alumina, but in my own work I find that it is desirable to make the distinction. I could cite an illustration that would bear out that point, but the example would not have any particular bearing on the subject of this paper.

B. M. LARSEN.—Dr. Hoyt's question is pertinent. Any attempt to distinguish accurately between different oxides in an analysis of this kind would be likely to overstep the mark. In the set-up used by Mr. Reeve (p. 82, this volume), the atmosphere is very low in oxygen pressure, and theoretically any oxide can be reduced. That brings in another complicating factor which is not mentioned in our paper, the fact that the rate of reduction is not merely a question of the chemical substances involved but also of the relative sizes of the oxide particles. Probably in our case, and in the case of the method mentioned by Dr. Hoyt, some of the manganese oxide present exists in very finely divided particles, which probably are reduced with the iron-oxide oxygen.

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† Research Metallurgist, A. O. Smith Corporation.

C. H. HERTY, JR.,* Pittsburgh, Pa.—I should like to comment on Dr. Hoyt's question. In 1919, Oberhoffer and Von Kiel tried to differentiate. They were unsuccessful because they got simultaneous reduction. In addition to the complication Mr. Larsen pointed out, there is the complication that there may be FeO particles, MnO particles, and a solid solution of MnO and FeO which would change the pressure needed.

* Director of Research, Mining and Metallurgical Advisory Boards to the Carnegie Institute of Technology.

Improvements in the Vacuum Fusion Method for Determination of Gases in Metals

BY LEWIS REEVE,* MILWAUKEE, WISCONSIN

(Detroit Meeting, October, 1933)

As part of a program of investigation of the properties of electric arc welds carried out in the laboratories of the A. O. Smith Corporation, considerable work has been done on the determination of the oxygen, nitrogen and hydrogen content of different types of weld metal, employing for this purpose the so-called "vacuum fusion method." It is the purpose of this paper to describe certain improvements that have been introduced in this method of determining the gas content of metals, with particular references to the steel specimens examined in this investigation.

The method and apparatus used at the beginning of the investigation were essentially those of the Bureau of Standards as described by Vacher and Jordan.¹ Later a number of changes were introduced which resulted in more rapid evacuation of the graphite crucibles employed and which enabled larger volumes of gas to be dealt with than could be handled conveniently in the Bureau of Standards equipment. In addition, the analyzing of the gases evolved from a melt in the same apparatus as collected was abandoned in favor of analysis outside the equipment using standard methods of gas analysis. The time required for gas analysis in the apparatus itself, as described by the Bureau of Standards, was found to be considerable, and during this time the rest of the equipment was tied up, preventing its use for the analysis of further steel samples. As a result of the modifications introduced, the time required for the analysis of a steel sample for gas content was reduced from about 8 hours to less than 3 hours.

Subsequently, the whole procedure of melting the sample and collecting the gases evolved was modified so as to enable a distinction to be drawn between the easily reducible oxides such as iron oxide and the more stable oxides such as silica and alumina. At the same time evidence was obtained indicating the probable existence in the steels of other nitrides than those of iron alone and making possible their quantitative determination.

* Metallurgical Department, A. O. Smith Corporation.

¹ Vacher and Jordan: U. S. Bur. Stds. *Jnl. of Research* (August, 1931) 375-401.

APPARATUS

The apparatus is shown in Fig. 1. The set-up consists essentially of:

1. An induction furnace and water-cooled coil *A* and a suitable vacuum furnace tube *B*. The latter was made of glazed vitreosil and was about 10 in. long and 1.4 in. internal diameter. A brass water-cooled head *C* was sealed to the tube with sealing wax. The head was provided with a window *D* sealed at the outer edges by a ground joint and vacuum grease. A smaller quartz window was sometimes mounted below *D* in a suitable holder and acted as a guard against flying particles, a precaution necessary with samples evolving large quantities of gas which caused the melting to be very wild. A silica guide tube projected downward into the furnace tube and served to guide the steel specimen *E* into the graphite crucible *G*. Between the graphite crucible and the outer vitreosil tube there was inserted a sillimanite protection screen. The design of the crucible and its method of support in the furnace tube will be described later.

2. Pumping equipment consisting of the mercury diffusion vacuum pump *K* connected via stopcock 9 to another mercury pump and to a mechanical oil pump (not shown in the drawing).

3. A McLeod gage *H* with multiple compression chambers for measuring pressures between 0.0005 and 20 mm. mercury, together with an ordinary U-tube manometer *O* for pressures up to about 130 mm. mercury.

4. Gas-collection reservoirs *L* and *M* as shown, which are used in the manner described later.

5. A Topley gas-collecting pump *T* connected to stopcock 6.

6. The necessary glass tube connections and stopcocks shown. The latter were specially selected and lubricated with high-quality vacuum grease.

Design and Method of Supporting Graphite Crucible in Furnace Tube

After considerable experimenting, the most suitable method of supporting the crucible in the furnace was found to be as shown in Fig. 1, and in more detail in Fig. 2. The crucible is supported by the flange *R* from the top of the sillimanite tube, and except for this support there is no contact whatever between the graphite crucible and the remainder of the refractory material in the furnace; in particular, there is no contact at the highly heated lower portion of the crucible. As originally used in accordance with the Bureau of Standards equipment, the crucible rested at its base on a refractory plug, for which magnesia, alundum and zirconia were tried out. Under these conditions, the hot graphite crucible, particularly during the initial evacuation at temperatures exceeding 1700° C., reacted with the plug and evolved considerable quantities of carbon monoxide; and it was only after the plug had been partially carburized that this reaction was slowed down to a sufficient

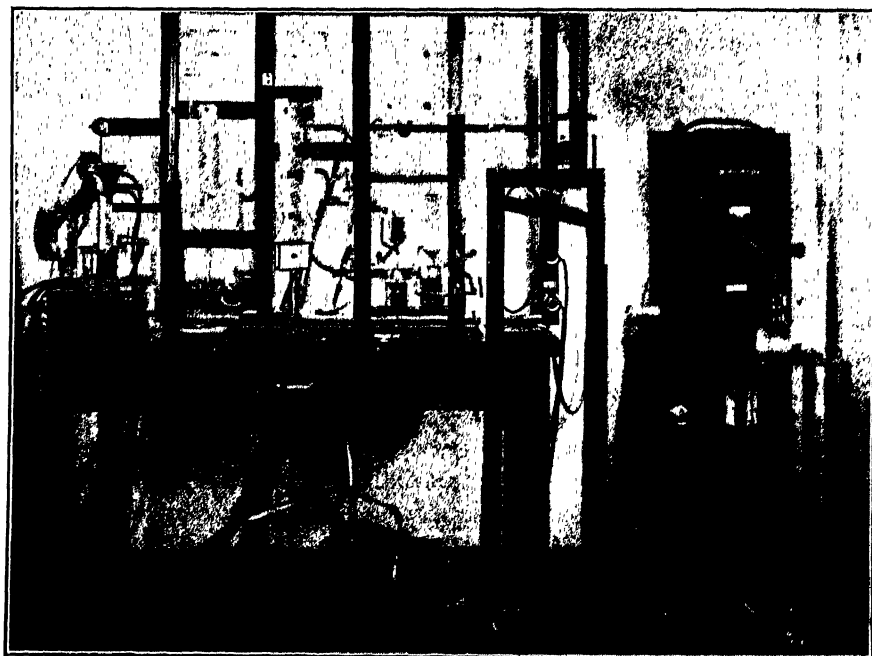
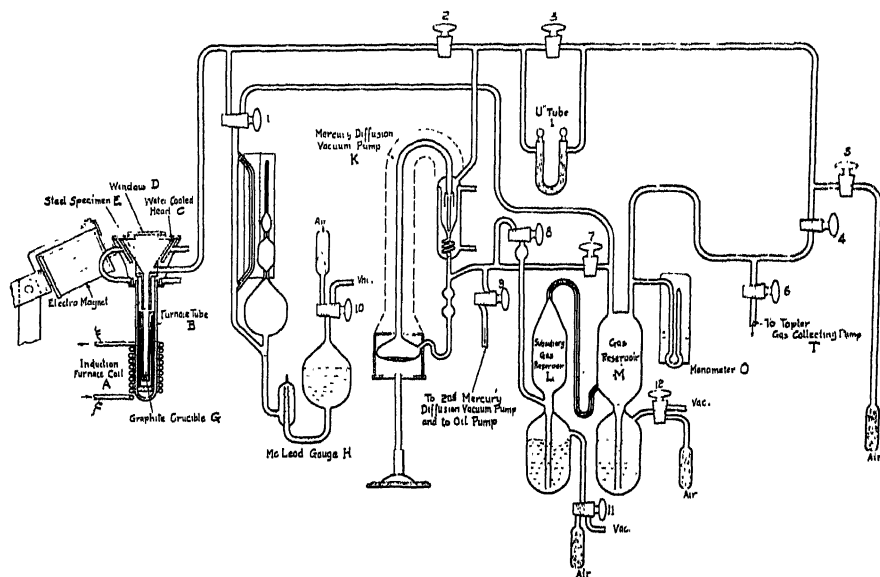


FIG. 1.—APPARATUS FOR DETERMINING GASES IN STEEL BY VACUUM-FUSION METHOD.
(Modified Bureau of Standards.)

extent to permit proceeding with the vacuum melt. The time required for the initial evacuation of the crucible was thus unduly prolonged, requiring from 3 to 8 hr., depending upon whether an old or new refractory plug was employed. After the substitution of the suspended type of crucible the time required to evacuate the crucible to a base pressure of 0.05 mm. and less at 1720° C. was reduced to about 60 min. The writer is indebted to Dr. J. J. Thompson of the Metallurgical Analytical Laboratory of the A. O. Smith Corporation for this excellent suggestion.

The term "base pressure," as just used, is employed in the sense as defined by the Bureau of Standards;² that is, the pressure in the furnace tube with the pumps in operation. The blank gas evolved by the crucible after such an evacuation would usually be less than 1 c.c. per $\frac{1}{2}$ hr. at 1570° C., corresponding to less than 0.002 per cent of oxygen on a 25-gram sample. A correction for this blank gas is applied to the final results in the manner described later.

Method of Collecting Gases

The gases collected from a vacuum fusion would be stored in gas reservoirs L and M , of which M is the main reservoir, L being really a modified form of a Topley pump. This arrangement differs from that employed by the Bureau of Standards, where the gas reservoirs consist simply of two glass

bulbs of about 600 to 700 c.c. capacity connected to the remainder of the equipment by suitably arranged tubing and stopcocks.³ The reason for the modifications introduced lies in the effect of excessive back-pressure upon the working of mercury diffusion vacuum pumps. In the Bureau of Standards equipment, if the pressure of the gases collected in the reservoirs were to exceed 10 to 15 mm., gas would

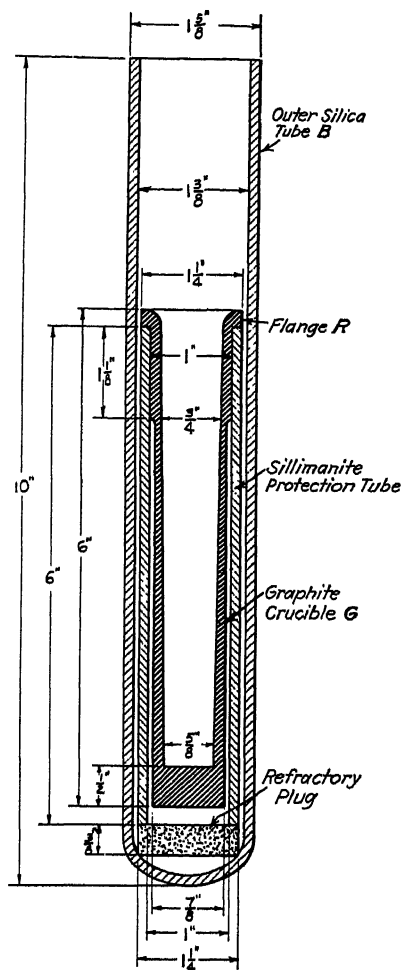


FIG. 2.—METHOD OF SUSPENDING CRUCIBLE IN FURNACE TUBE.

² Reference of footnote 1, 385.

³ Reference of footnote 1, 378.

leak back to the furnace past the mercury diffusion pump, such a pump being incapable of working efficiently when the back-pressure exceeds this amount. In the determination of the oxygen and nitrogen content of welds, where the gas volumes dealt with were often considerably larger than in the steel samples discussed in the Bureau of Standards report, and where the gas pressures would often exceed 50 mm., it was necessary to seal off this gas from the pumps more efficiently than in the Bureau of Standards apparatus. This was carried out with the aid of the subsidiary gas reservoir *L* already referred to. At the beginning of a determination gas would be delivered by the pump *K* to reservoir *M* via stopcock 7, while reservoir *L*, previously evacuated, would be kept closed off at stopcock 8. When the gas pressure in *M* reached about 5 mm., stopcock 7 would be closed and stopcock 8 opened. Periodically after this, the gas collected in *L* would be pushed over into *M* by allowing air pressure to enter through stopcock 11 and thus forcing mercury upwards into *L* from the reservoir below it. As soon as mercury passed over the top of *L* into the capillary tube connecting it with *M*, the mercury in *L* would be lowered again to the position shown in Fig. 1 by turning stopcock 11 to connect with vacuum. A thread of mercury would be left behind in the capillary tube, effectively sealing off the gas in *M* from reservoir *L*. Gas would once again be delivered by the pump through stopcock 8 into *L*, and the process of pushing it over into *M* would be repeated. In this way large quantities of gas—up to about 130 mm. pressure—could be collected in *M* without allowing the back-pressure on the pump to rise to an unsafe amount.

After the gas evolved by the steel specimen was safely stored in *M*, it was pumped via stopcock 6 into test tubes over mercury by means of Topley pump *T* and then subjected to standard methods of gas analysis, using a mercury Orsat gas-analysis apparatus with compensated and calibrated burette.⁴ This method of analysis was faster than analysis in the equipment itself. Handling small samples was facilitated by diluting with known volumes of pure nitrogen in the gas-analysis burette.

Method of Supporting Steel Specimen in Water-cooled Head

The steel sample, in the preliminary stages of a determination, when the graphite crucible was being evacuated, was supported against the cool wall of the brass head *C* by means of electromagnet *F*. By de-energizing this magnet the specimen could be dropped into the hot crucible below. Subsequently another method of support was devised for non-magnetic samples, in which the specimen was maintained in place on a tiny shelf that could be swung out of place by means of a steel rod actuated by a magnet.

⁴ See sampling and examination of mine gases. U. S. Bur. Mines *Bull.* 197, 43-54.

METHOD OF CARRYING OUT A VACUUM FUSION ANALYSIS

Apart from the differences in the equipment described above and in the method of analyzing the gases evolved, the method of carrying out a steel analysis is in all important respects identical with that described by the Bureau of Standards.

The specimen *E*, usually in the form of a small cylinder about 11 mm. dia. and 35 mm. long, weighing about 26 grams, was placed inside the water-cooled head *C* of the furnace tube in the position shown in Fig. 1 and kept in that position by means of the electromagnet. The specimen had been machined clean, using cutting tools only, without any abrasives, and had been stored in a clean, dry test tube in a dessicator. After weighing, it was gripped in a specially shaped pair of clean tongs, washed with ether to remove oil and grease, and placed inside the furnace head as described, without being touched by hand. The window *D* was then placed in position and sealed gastight with vacuum grease. The whole equipment was then evacuated (furnace kept cold) for about 15 min.; the pumps were then closed off and the apparatus tested for major leaks. The induction furnace was started and pumping was continued via stopcock 9 with the graphite crucible maintained at a temperature of 1720° C. Evacuation proceeded until the pressure in the furnace tube fell to at least 0.1 mm. Owing to the improvements in mounting the crucible as described, and the introduction of larger mercury-vapor pumps, this base pressure at 1720° C. was subsequently reduced to 0.05 mm. in an evacuation time of about one hour. At the end of this evacuation period, the temperature was reduced to 1570° C., which is the actual operating temperature at which the steel sample is ultimately melted. The pressure in the furnace would fall as a result to about 0.005 mm. Stopcock 9 would then be closed and the gas evolved by the crucible during a period of 30 min. at this temperature collected and stored in a test tube over mercury as described. This gas is referred to as the blank for the crucible and has averaged in our determinations about 1 c.c. in volume, about the same amount as obtained by the Bureau of Standards.⁵ After removing this blank gas, the electromagnet would be de-energized and the steel specimen would drop into the graphite crucible. The temperature would fall momentarily, but within a few minutes it would be back again at 1570° C., and the steel sample would be completely melted. Gas would be evolved more or less rapidly, depending upon the gas content of the sample; in nearly all cases, however, more than 75 per cent of the gas would be evolved within 15 min. of dropping the sample and 90 per cent within 30 min. Evacuation and collection of the gas was usually continued for 60 min. from the time of dropping the sample. The gases were

⁵ Reference of footnote 1, 386.

first stored in gas reservoir *M* and then transferred to test tubes over mercury in the manner described. They were subsequently analyzed for carbon dioxide, oxygen, hydrogen, carbon monoxide and nitrogen, from which the percentage by weight of the oxygen, nitrogen, and hydrogen in the steel sample was calculated, allowance being made for the blank gas evolved by the crucible.

Procedure When Starting a Fresh Determination

Three furnace tubes were available and a fresh one was always ready to replace the old one at the end of a run. Between runs the used furnace tube would be completely dismantled and the outer quartz tube, the guide tube, and the sillimanite tube cleaned in acid, washed and dried, and finally reassembled in readiness for another determination. A fresh graphite crucible was used for each determination and a fresh sillimanite tube about every six determinations. The outer quartz tubes last from 20 to 30 runs, after which they are apt to crack and are therefore replaced.

MODIFIED VACUUM FUSION METHOD FOR FRACTIONAL ANALYSIS OF INCLUSION AND GAS CONTENT OF METALS

At an early stage of the work on the gas and inclusion content of weld metal it became apparent that the iron and possibly manganese oxides were considerably more harmful to the physical qualities of the metal than were alumina and silica. It became desirable therefore to evolve methods for the separate determination of these oxides. Electrolytic extraction methods suitable for silica and alumina were available which, in conjunction with the total oxygen by the vacuum fusion process, should give, by difference, the oxygen as FeO and MnO. Some work on these lines was carried out, but certain observations suggested to the writer the possibility of a simpler process, which would analyze all these oxides in a single operation. It was observed that steels known to contain large amounts of iron oxide were reduced much more rapidly in the graphite crucible of the vacuum fusion apparatus described than were steels deficient in this oxide. The effect of temperature upon the reduction of oxides by carbon was considered. It was known that FeO was reduced by carbon at temperatures well below 1000° C., and that oxides such as silica and alumina were more difficult to reduce and required considerably higher temperatures.

It was also known in a general way that in order to completely reduce *all* the oxides present in a steel sample by the vacuum fusion method it was necessary to employ working temperatures approaching 1600° C., and that the incomplete results obtained at lower temperatures were probably due to incomplete reduction of the more refractory oxides.⁶

⁶ Hessenbruch and Oberhoffer: *Archiv f. Eisenhüttenwesen* (1928) 9, 595.

It seemed likely, in view of these considerations, to distinguish between the different oxides present as inclusions in a steel sample by a process of fractional reduction at increasing temperatures. In order to determine the feasibility of such a procedure, tests were carried out upon the following steel samples:

1. A highly oxidized melt of ingot iron.
2. Oxidized ingot iron deoxidized with aluminum.
3. Oxidized ingot iron deoxidized with ferrosilicon.
4. Oxidized ingot iron deoxidized with ferromanganese.

In each case a quantity of pure tin, from 50 to 100 per cent of the weight of the steel specimen, was added to act as a flux. The results reported in Table 1 were obtained at the temperatures shown, using the vacuum fusion equipment described.

TABLE 1.—*Test Results of Fractional Vacuum Analysis of Steel Samples Containing Known Oxide Inclusions*

Specimen No.	Description*	Temp. of Reduction, Deg. C.	Gases Evolved, Percentages by Weight		
			O ₂	N ₂	H ₂
1	Oxidized ingot iron melt..	1050	0.165		0.00056
		1300	0.002		
		1570	0.010	0.004	0.00054
2	Oxidized ingot iron deoxidized with aluminum.	1050	0.006	0.003	0.0004
		1300			
		1570	0.039	0.002	
3	Oxidized iron deoxidized with ferrosilicon.	1050			
		1200			
		1300	0.058	0.002	0.0006
		1570			
4	Oxidized iron deoxidized with ferromanganese.	1050 to 1150	0.073	0.007	0.0028
		1300	0.008		0.0001
		1570	0.030	0.004	0.0006

CHEMICAL ANALYSIS OF SPECIMENS

Specimen No.	Percentages			
	C	Si	Mn	Al
1	0.025	0.01	Trace	Trace
2	0.025	0.02	Trace	0.186
3	0.034	0.71	Trace	
4	0.025	0.01	0.35	Trace

* The specimens of oxidized ingot iron mentioned do not refer to specimens from the same melt.

Examination of the results in Table 1 indicates that iron oxide, as in specimen 1, was reduced by carbon at 1050° C.; manganese oxide, as in specimen 4, was reduced at 1050° to 1150° C.; silicon oxide, as in the silicon-killed ingot 3, gave no gases at these low temperatures and was not decomposed with any rapidity until 1300° C.; and, finally, in the aluminum-killed ingot 2, in which, presumably, most of the oxygen was present as alumina, very little gas was evolved until temperatures of over 1500° C. were attained. Most specimens appeared to contain a little alumina, particularly ingot 4.

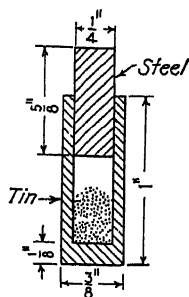


FIG. 3.—TIN CAPSULE.

Experiments on Reduction of Powdered Oxides and Silicates

Further substantiation of the accuracy of these decomposition temperatures was obtained in a series of experiments in which small quantities of powdered oxides of known compositions were placed in small tin capsules closed by a steel plug in the manner indicated in Fig. 3, and submitted to analysis in the vacuum fusion equipment. The results of some of these experiments are shown in Table 2.

TABLE 2.—*Reduction of Powdered Oxides by Carbon*

Oxide	Temperature of Reduction, Deg. C.	Percentage Yield of Oxygen Collected as CO
Iron oxide.....	1000-1050	97.3
Manganous oxide.....	1150	86.9
Silica.....	1300	100.0
Alumina.....	1550-1600	75.0

Very slow reduction was observed at temperatures about 50° C. below those quoted in Table 2. The oxygen yields calculated from the CO evolved were not always 100 per cent and, moreover, were liable to be erratic in repeat experiments, but the temperatures of reduction were always substantially as shown. When low results were obtained, no improvement followed by raising the temperature, gas evolution for a particular oxide being complete at the temperatures indicated in Table 2.

This quantitative inaccuracy has been observed by other investigators,⁷ and must be ascribed to physical loss of the powdered oxide by sputtering and similar effects, together with the loss of CO by reaction with metallic vapors, particularly aluminum. It should be remembered in this connection that the relative concentration of oxide to steel in these tests was considerably greater than the inclusion content of even the dirtiest steel. It is interesting to record that very much lower results were obtained when the oxides were enclosed in a tin capsule alone, with-

⁷ Diergarten: *Archiv f. Eisenhüttenwesen* (1930) 9, 578-579.

out the steel plug shown in Fig. 3. (The capsule was closed in this case by nipping the open mouth with a pair of pliers.) The presence of iron facilitates the reduction, probably by helping the solution of carbon from the walls of the graphite crucible. The most important result of these experiments was to confirm the reduction temperatures already determined in connection with the experiments reported in Table 1.

Some results obtained with a manganese silicate of approximate composition $\text{MnO} \cdot \text{SiO}_2$ should be mentioned. The procedure employed in the reduction of this material was somewhat different from that already described. In order to obviate the necessity for correcting for the oxygen content of the steel plug, this was dispensed with and the silicate was placed in a pure tin capsule. The necessary iron was put inside the graphite crucible in the form of 10 grams of electrolytic iron, which was thoroughly degasified during the initial evacuation of the crucible at 1720°C .

The temperature was then reduced to 1150°C . and the tin capsule containing the manganese silicate was dropped into the crucible.

In the first experiment carried out in this manner the silicate "packed" together as a clot of compacted powder on one side of the crucible and remained there very much colder than the tin-iron alloy below it. The rate of reduction was exceedingly low and it did not seem advisable to raise it by increasing the furnace temperature.

The experimental procedure was therefore modified again as follows:

1. One gram of graphite powder was added to the iron at the bottom of the graphite crucible and was subjected to the preliminary evacuation at 1720°C . Some of this powdered graphite remained floating on top of the melt, mainly near the walls of the crucible.

2. About 0.5 grams of tin filings was mixed with the manganese silicate in the tin capsule. The tin filings prevented the compacting of the manganese silicate and helped to scatter it more uniformly over the surface of the melt. The silicate also became intermingled with the graphite powder and was reduced more quickly.

Results obtained in this manner are summarized in Table 3.

TABLE 3.—*Reduction of Manganese Silicate in Graphite Crucible*

Weight of manganese silicate, 0.0260 grams

Weight of electrolytic iron, 10.483 grams

Temperature of Reduction, Deg. C.	Weight of O_2 Collected as CO , Grams	O_2 in Silicate (from Chemical Analysis)		
		Form	Weight, Grams	Percentage Yield
1150	0.00258	MnO	0.00307	84
1300	0.00540	SiO_2	0.00598	90.5
1570	0.00040	CaO , MgO , Al_2O_3 , etc.	More than 0.00025	

In another run where the temperature for the first fraction was allowed to rise to 1200° to 1230° C., the MnO yield was too high and the SiO₂ yield too low by almost the same amount, indicating some reduction of SiO₂ at these temperatures. It is important that the temperature of the first fraction should not exceed 1170° C., and preferably not more than 1150° C.

The results reported in Table 3 verify the temperatures of reduction employed for the different oxides even when present in the form of silicates. The actual values obtained for the oxygen yields are satisfactory quantitatively. The experiments indicate, however, the difficulties encountered in attempting to duplicate the reduction of inclusions in a steel sample by means of experiments with powdered oxides.

Enough work has been done, however, to substantiate the conclusion that it should be possible to determine the distribution of oxygen among the different oxides in a steel sample by collecting separately the gas fractions evolved at certain temperatures. The most suitable values for the average run of steel specimens examined to date, including the weld samples investigated, were found to be: 1050° to 1150° C. for FeO and MnO; 1300° for SiO₂; and 1570° for Al₂O₃.

DETAILS OF PROCEDURE FOR FRACTIONAL DETERMINATIONS

Some of the more important details of procedure employed in such fractional determinations are as follows:

The steel sample, usually in the form of a cylinder 11 mm. in diameter, is tied to a piece of pure clean stick tin by means of a short piece of fine iron wire, resulting in a cylinder of approximately uniform diameter, about 35 mm. long. The approximate weights of average samples would be about 14 grams of steel and 8 grams of tin. The compound specimen is suspended in the water-cooled head *C* of the furnace tube *B* in the manner already described in connection with Fig. 1, and the graphite crucible is evacuated for about one hour at 1720° C. until the base pressure falls to 0.05 mm. or less. The temperature is then reduced to 1050° to 1075° C., and the specimen is dropped. The tin melts almost immediately, and within about 15 min. the steel alloys with the tin to produce a melt which in one case analyzed: tin, 31.8 per cent; carbon, 1.08 per cent. A rapid gas evolution at this low temperature is indicative of the presence of iron oxide. Manganous oxide, if present, gives off its oxygen much more slowly, and to hasten matters, it is advisable in such a case to raise the temperature to about 1150° C. This difference in rate of decomposition is very marked and is sufficient to distinguish between the two oxides. Curves 1 and 2 of Fig. 4 show the rate of reduction of iron oxide in the weld samples indicated, while curves 3 and 4 show the rate of evolution of gas from the reduction of manganese oxide in two steels deoxidized with manganese only. Although the amount of oxygen present is different in all the samples, the rate of reduction can be compared quantitatively by

noting the time required for a definite percentage of the reduction to take place, say 50 per cent. These times are indicated on the curves in Fig. 4 by the short vertical dotted lines. It will be noted that these times are approximately constant for the two samples containing iron oxide (15 and 12½ min. respectively) and also, but much longer, for the two samples containing manganese oxide (44 and 60 min. respectively) indicating a much slower rate of reduction of manganese oxide at 1150° C. than of iron oxide at 1050° C. (The two oxides could probably be distinguished even more clearly by analyzing for FeO at still lower temperatures than 1050° C., say 950° C.) The gas evolved at these temperatures is collected in the usual manner until the base pressure falls to about

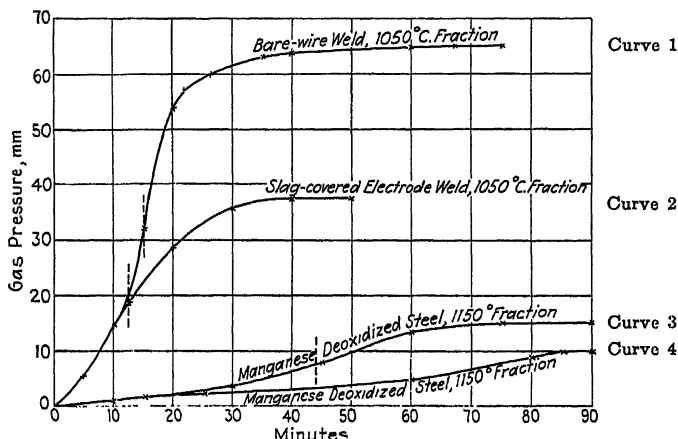


FIG. 4.—RATE OF REDUCTION OF IRON AND MANGANESE OXIDES IN STEELS.

0.003 mm. The time required for this to occur may be as low as 30 min. in the case of a sample low in iron oxide to as much as 2 hr. in the case of a sample high in manganous oxide. The average time is about 60 minutes.

The temperature is then raised to 1300° C., and if any SiO_2 is present, a fresh gas evolution commences and is allowed to continue until the base pressure falls to about 0.004 mm. This again takes, on the average, about 60 min. This gas is collected separately. Finally, the furnace temperature is raised to 1570° C., and any gas evolved from Al_2O_3 and similar oxides is collected until the base pressure falls to about 0.006 mm. This gas constitutes the final gas fraction and takes again about 60 min. to collect from the crucible. Total time for a fractional analysis, including the preliminary evacuation of the crucible, averages about 5 hours.

These gas fractions are analyzed separately, and from the results the weight percentages of FeO , MnO , SiO_2 and Al_2O_3 present in the original steel sample are calculated. Blank corrections for the gas evolved by the crucible at the different temperatures are applied on the basis of the average results obtained in a number of runs with an empty crucible in

which the gases evolved in one hour at the different temperatures were separately collected and analyzed. The blanks at 1100° and 1300° C. correspond to less than 0.5 c.c. gas per hour; the blanks at 1570° C. are larger but quite regular at about 1.3 c.c. per hour. No corrections are applied for the gas evolved by the tin itself, separate determinations having shown that this quantity was even lower than the gas blanks from the crucible.

The time-pressure curves for some typical weld specimens analyzed by the fractional vacuum fusion method are shown in Fig. 5. Approxi-

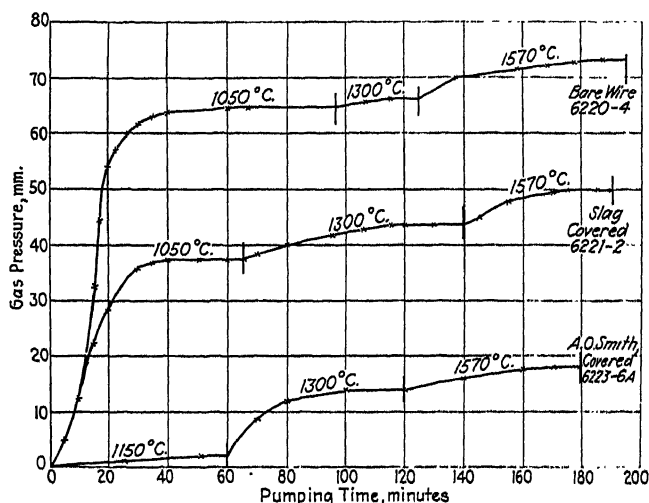


FIG. 5.—EVOLUTION OF GASES FROM VACUUM FUSION OF ALL WELD METAL AT DIFFERENT TEMPERATURES.

mately 12 grams of weld metal were used in each determination. It will be observed that at each operating temperature gas evolution proceeds at a more or less rapid rate initially, sloping off until finally the pressure remains constant, indicating the end of reduction at that particular temperature. On raising the temperature to the next operating value, a further burst of gas evolution takes place to reach again a constant pressure value.

In connection with these curves, note the marked difference in the gas pressure for the first fraction of the weld made with the A. O. Smith covered rod as compared with the first fractions for the bare wire and slag-covered rod welds. This corresponds to the very low iron and manganese oxide content of the A. O. Smith weld as compared with the extremely high iron oxide content of the welds produced with bare wire or slag type electrodes. Note also the much lower total gas content of the A. O. Smith weld. The calculated results corresponding to these curves are shown in Table 4.

TABLE 4.—*Typical Results for the O₂, N₂ and H₂ Content of all Weld Metal, Using the Fractional Vacuum Fusion Method of Analysis*

Specimen No.	Description	Chemical Analysis, Per Cent			Fractional Gas Analysis				
		C	Mn	Si	Temp., Deg. C.	O ₂ as	Per Cent	N ₂ , Per Cent	H ₂ , Per Cent
6220-4	Bare wire weld	0.021	0.09	0.014	1050	FeO	0.282	0.159	0.00025
					1300	SiO ₂	0.0003	0.0077	
					1570	Al ₂ O ₃	0.022	0.0141	
6221-2	Weld made with slag-type electrode	0.038	0.09	0.042	1050	FeO	0.208	0.009	
					1300	SiO ₂	0.032	0.010	
					1570	Al ₂ O ₃	0.017	0.017	
6223-6A	Weld made with A. O. Smith covered electrode	0.08	0.57	0.25	1150	MnO	0.005	0.001	0.00026
					1300	SiO ₂	0.058	0.002	0.00016
					1570	Al ₂ O ₃	0.009	0.004	0.00014

COMPARISON OF RESULTS OBTAINED BY FRACTIONAL VACUUM METHOD WITH OTHER METHODS OF DETERMINING INCLUSIONS IN STEEL

The results obtained by the fractional vacuum fusion method have been compared with results obtained by other methods in a number of ways:

1. It has been found in all the cases tested to date that the total gas content of a sample, as determined by adding together the gas quantities in the separate fractions, agrees very well with the total gas content of the same steel as determined by the ordinary vacuum fusion at 1600° C. Two typical examples are shown in Table 6. The only important difference is with regard to hydrogen, which is discussed more fully later. It follows that no additional experimental errors are involved in the fractional method with regard to the *total* gas evolved than are inherent in the ordinary vacuum fusion method.

2. Results obtained by the fractional vacuum fusion method for the oxygen distribution in a steel specimen have been checked qualitatively in a very large number of cases by metallographic examination of corresponding specimens. In so far as the type of oxide inclusions could be identified by microexamination, the results were in complete agreement with those yielded by the fractional vacuum fusion. Thus, where the microexamination indicated a predominance of the highly siliceous type of inclusion, the fractional analysis showed a predominance of oxygen in the second, or SiO₂, fraction. The detailed results of the metallographic examination of many of these specimens is to be reported in a separate paper by Dr. S. L. Hoyt, of the A. O. Smith Metallurgical Laboratory.

3. In a few cases comparisons have also been made between the results of fractional vacuum analysis and those obtained by electrolytic extrac-

tion using the method described by Fitterer⁸ applied to portions of the same steel specimens. Some of the comparative results obtained in this manner are shown in Table 5.

TABLE 5.—*Comparison of Results Obtained by Fractional Vacuum Fusion Method and by the Electrolytic Extraction Method*

Specimen No.	Fractional Vacuum Fusion			Electrolytic Extraction		
	1050° C. -1150° C.	1300° C.	1570° C.	O ₂ as MnO	O ₂ as SiO ₂	O ₂ as Al ₂ O ₃
8911-3	0.0	0.043	0.029	0.0	0.055	0.038
8911-4	0.008	0.044	0.011	0.004	0.056	0.019

There is fair agreement between the 1300° C. fraction (O₂ as SiO₂) and the oxygen as SiO₂ given by electrolytic extraction. The 1570° C. fraction (O₂ as Al₂O₃) appears to be definitely low as compared with the oxygen as Al₂O₃ by electrolytic extraction, but the vacuum fusion method is known to give low results for this oxide unless it is present in extremely small amounts. The electrolytic extraction method is unable to determine oxygen as FeO and its results for MnO are doubtful, hence no comparison is possible as regards the first fraction, although the results appear to be of the right magnitude.

In making these comparisons it should not be forgotten that divergences of almost the same magnitude have been found for adjacent specimens of similar steels using either of the analytical methods under consideration. This must undoubtedly account for some of the discrepancies, at least as far as SiO₂ is concerned, since 100 per cent yields have been obtained for this oxide by the vacuum fusion method both by the writer and by other investigators.⁹

In general, it appears that, within the limits of accuracy of the vacuum fusion method, the fractional method described is likely to give a reasonably accurate idea of the distribution of the oxygen among the different oxides present in a steel sample, and to do this moreover in what is essentially one analytical determination. In this respect it is suggested that the method is likely to give a better picture of this distribution than the methods used hitherto, which have determined FeO plus MnO as the difference between total oxygen by the vacuum fusion method and oxygen as SiO₂ and Al₂O₃ by the electrolytic or acid extraction method. The fractional method gives FeO and MnO directly, and also, in the same determination, SiO₂ and Al₂O₃.

⁸ Fitterer: *Trans. A.I.M.E.* (1931) **95**, Iron and Steel Div., 196.

⁹ See page 90 of this paper; also reference of footnote 1, 393.

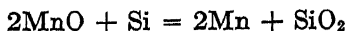
POSSIBLE INACCURACIES OF THE FRACTIONAL VACUUM FUSION METHOD

The normal experimental error of the vacuum fusion method for uniform steel samples may be taken as being about 0.002 per cent for O_2 and N_2 and about 0.0002 per cent for H_2 , corresponding to approximately 0.25 cu. cm. of each of these gases on a 10-gram steel sample. In addition, errors due to the disturbing effect of excess manganese or aluminum may enter as described by Jordan and Vacher.¹⁰ In connection with most steel samples errors due to manganese are eliminated by using a fresh graphite crucible for each determination and by maintaining as high a vacuum as possible during the collection of the gases from the melt. Errors due to aluminum are likely to enter if the alumina oxygen exceeds 0.01 per cent or metallic aluminum exceeds 0.3 per cent. A minor source of error arises if Na_2O is present. This volatilizes and is not estimated. The amount is usually very small.

One other possible source of error must be considered with particular reference to the fractionation method. This lies in the possible displacement of equilibria at each of the operating temperatures. Thus, consider the deoxidation equilibrium between silicon and iron oxide:



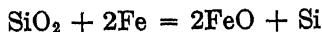
If the steel sample that is being analyzed is to be regarded as having attained equilibrium with respect to this reaction at the temperature at which it was originally deoxidized, say $1600^\circ C.$, then, in theory, it will not be in equilibrium at the temperature of the first fraction ($1100^\circ C.$) in the analytical method under discussion. Since this deoxidation of FeO is an exothermic reaction, the equilibrium will tend to be displaced towards the right at the lower temperature; that is, the sample will tend to analyze too low in FeO and too high in SiO_2 . Similarly with regard to the reaction



and the corresponding deoxidations by aluminum.

In the special case of weld metal deposited at exceedingly high temperatures, the metal may not have been in equilibrium with regard to these deoxidation reactions even when originally deposited, in which case the tendency to analyze too low in FeO and MnO may be even more marked.

On the other hand, during the analysis of the first fraction, as the FeO and MnO are being reduced by the carbon, there should be in theory a tendency for the reverse reaction



to take place, thus counterbalancing to a certain extent the effect of the previously considered reactions. The net result, obviously, will depend

¹⁰ Reference of footnote 1, 389-395.

upon the relative velocities of these reactions at the comparatively low temperature of the first fraction.

Similar considerations will apply if aluminum is present in the steel, and there may be some tendency for the displacement of equilibria in that case both in the first and in the second fractions.

Insufficient data are available to determine the importance of these possible equilibrium displacements. It is doubtful whether they are of sufficient importance to interfere vitally with the general interpretation of the results obtained. A comparison with the results of the electrolytic extraction method would probably be the easiest way of deciding the question. As already pointed out, in the few cases in which this has been done, there has been reasonably good agreement with the fractional vacuum fusion method. It would be desirable, however, for a more extensive comparison to be made.¹¹

NITROGEN AND HYDROGEN DETERMINATIONS BY FRACTIONAL VACUUM FUSION

The results shown in Table 1 indicate that, contrary to what might have been expected, the nitrogen and hydrogen in the steel samples there under consideration were not all evolved in the first fraction; some of these gases were evolved in subsequent fractions. A similar conclusion may be drawn from the results in Table 4. There is, on the whole, a tendency for the major portion of the hydrogen to be evolved in the first fraction, particularly from samples rich in this gas. This tendency will be considered in more detail later. The distribution of the nitrogen is, if anything, towards the higher temperature fractions, although there are marked exceptions, as in the nitrogen in the bare wire weld metal, sample 6220-4, Table 4, which was evolved mainly in the first fraction.

In considering these results, it should be remembered that the collection of the gases from any fraction is not considered complete until the base pressure (the pressure in the furnace) falls to the amount corresponding to the pressure given by the crucible itself at the same temperature

¹¹ Since the completion of this paper, some extremely interesting determinations have been made on the gas content of a gray iron analyzing 3.0 to 3.2 per cent C, 1.7 per cent Si, 0.4 per cent Mn, which indicate that the extent of deoxidation of FeO and MnO by silicon at the temperatures of the first fraction is negligible. Despite the high silicon content of this iron, some of the specimens were badly oxidized and analyzed as high as 0.047 per cent O₂ as FeO + MnO (of which much was FeO) while the O₂ as SiO₂ averaged only 0.007 per cent. Microscopical examination indicated the presence of some such small quantity of SiO₂. It is apparent from these results that at the temperature of the first fraction (up to 1150° C.) no appreciable deoxidation of FeO and MnO by silicon could have occurred during the period of the analysis (about one hour). The results indicate also the possibility of the existence of badly oxidized gray irons in which the normal course of deoxidation has been stopped at a point very far from equilibrium.

(0.003 to 0.006 mm.). That is, the first fraction includes all the gas the molten steel-tin sample can evolve at 1050° to 1150° C. No more gas, apart from the small amount from the crucible itself, is being produced at the stage when the temperature is raised to 1300° C. Hence, in the same way as for the oxygen, it must be concluded that any nitrogen evolved at 1300° C., and probably, to a lesser extent, any hydrogen evolved at the same time (see later), must be, somehow, differently associated with the steel than the same gases at 1050° to 1150° C.; similarly for the nitrogen and hydrogen, if any, evolved at 1570° C.

In regard to nitrogen, the question is immediately raised whether we are not dealing here with the thermal decomposition of a series of nitrides of increasing stability, requiring, therefore, higher and higher temperatures for decomposition. It is known that iron and probably manganese nitrides are easily decomposed at temperatures below 1000° C., and it is reasonable to assume that the nitrogen collected in the first fraction, at temperatures up to 1150° C., includes the nitrogen from these nitrides. With regard to other possible nitrides, it is stated by Jean Rieber¹² that aluminum nitride decomposes above 1400° C. According to Hincke and Brantley¹³ silicon nitride Si_3N_4 has a decomposition pressure of 5.5 mm. at 1529° C. But other nitrides of silicon are known for which corresponding data are lacking.

While considerably more investigation is required to support a definite conclusion, it is suggested tentatively that the nitrogen evolved at 1300° C. is associated with the silicon, and at 1570° C. is probably combined with the aluminum in the steel samples under investigation. A study of the nitrogen distribution in special nitriding steels by means of this fractional vacuum fusion method should be of considerable interest.¹⁴

Hydrogen Content of Steels

The hydrogen content of steels as determined by fractional vacuum analysis requires discussion. It has already been pointed out that if the oxygen and nitrogen content of a given steel specimen are determined, first by the ordinary vacuum fusion method and then by adding together the separate fractions in the fractional method, the results invariably agree within reasonable limits. But the same is not true for the hydrogen content as determined by the two methods; the fractional method usually gives considerably higher results. Some examples are shown in Table 6.

¹² J. Rieber: Doctor's Thesis, Technische Hochschule, Hanover, 1930. *Metals & Alloys Abstracts* (1932) 326.

¹³ Hincke and Brantley: *Jnl. Amer. Chem. Soc.* (1930) **52**, 48.

¹⁴ Since the preparation of this paper, the work of Fry on the decomposition of nitrided metals in vacuo at temperatures up to 1000° C. has appeared (May, 1932, meeting of Iron and Steel Inst., London). Iron nitride shows a maximum of decomposition at 600° C., manganese nitride at 700° C., while aluminum nitride does not decompose even at 1000° C. No results are reported for silicon nitride.

TABLE 6.—*Comparison of Results for Oxygen, Nitrogen, and Hydrogen Content of Steel Samples Determined by Ordinary Vacuum Fusion and by Fractional Vacuum Fusion*

1	2	3	4	5		6	7	8
Specimen No.	Description	Percentages						
		Ordinary Vacuum Fusion				Fractional Vacuum Fusion		
		O ₂	N ₂	H ₂		O ₂	N ₂	H ₂
8882	Weld made with lightly coated (washed) electrode.				FeO	0.208	0.114	0.00059
					SiO ₂	0.007	0.033	0.00059
					Al ₂ O ₃	0.012	0.009	0.00040
		0.218	0.159	0.0	Total..	0.227	0.156	0.00158
11614	Weld made with heavy covered electrode.				MnO	0.002	0.001	0.00025
					SiO ₂	0.045	0.004	0.00029
					Al ₂ O ₃	0.005	0.009	0.00010
		0.060	0.014	0.0	Total..	0.052	0.014	0.00064

The total O₂ and the total N₂ in columns 6 and 7 agree reasonably well with the corresponding figures for the same sample in columns 3 and 4, but the total hydrogen obtained by the ordinary method (column 5) is zero in both samples; whereas, by the fractional method (column 8), it is quite appreciable. It should be pointed out that 0.0006 per cent hydrogen on a 15-gram sample corresponds to approximately 1 c.c. of this gas. It also corresponds approximately to the solubility of this gas in pure iron just below the melting point.¹⁵

Such marked disagreement in the hydrogen by the two methods has been obtained consistently, the hydrogen by the fractional method being always considerably greater. It was thought at first that the larger hydrogen obtained by the fractional method might be due to hydrogen in the tin that was added. But this does not agree with a number of observations. First, blank determinations of the gas content of the tin itself showed that it was remarkably clean, containing about 0.0002 per cent hydrogen and about 0.002 per cent oxygen, these weight percentages corresponding to less than 0.2 c.c. of each of these gases in the weight of tin normally employed in a determination. Some of the steel samples analyzed in the presence of this tin contained more than ten times this amount of hydrogen. Secondly, the amount of hydrogen found in the steel samples examined varied considerably, from almost zero to as high

¹⁵ Luckmeyer Hasse and H. Schenk: *Archiv f. Eisenhüttenwesen* (1932) 210.

as 0.0036 per cent, the weight of tin employed remaining approximately constant. It can only be concluded that the ordinary vacuum fusion method does not yield all the hydrogen present in a steel sample, and that the presence of tin somehow favors the evolution of this gas, possibly by reducing the solubility of hydrogen in steel. In this connection, attention has been drawn by numerous investigators to the difficulty of removing all the hydrogen present in a steel even by the vacuum fusion process.

There is no evidence for the existence of stable metal hydrides except in a very few elements (such as tantalum and vanadium). It must, therefore, be concluded that the hydrogen found in the steel samples under examination must have been present in them in physical solution rather than in chemical combination. This is supported by the fact that in most of the samples containing appreciable quantities of hydrogen, the major portion of this gas was evolved in the first fraction. The results in Table 6 are hardly typical in this respect. A number of more representative results illustrating this point are shown in Table 7.

The greater part of the hydrogen in these samples was evolved at 1100° C., and comparatively small amounts only at 1300° and 1570° C. That is, the greater part of the hydrogen was driven off on the first melting of the metal, suggesting a comparatively weak attraction between metal and gas. The small amounts evolved in the later fractions may possibly be driven off by the sweeping action of the CO and N₂ evolved simultaneously. This method of gas evolution is entirely different from that of the carbon monoxide and nitrogen, which, depending upon the circumstances, may be evolved as a maximum in any one of the fractions, agreeing with the hypothesis that they are present in the metal as definite oxides and nitrides.

TABLE 7.—*Evolution of Hydrogen from Steel Samples*

Sample No.	Description	Percentage Hydrogen by Weight Evolved at		
		1100° C.	1300° C.	1570° C.
9473T	Welds made with heavy covered electrodes.	0.00105	0.00007	0.0
9472T		0.00182	0.00027	0.00024
9512T		0.00105	0.00008	0.0
9474T		0.00132	0.00013	0.00006
11653T		0.00106	0.00031	0.00027

CONCLUSION

A considerable amount of work has been carried out in the laboratories of the A. O. Smith Corporation upon the metallurgical significance of the results of the gas analysis of steels of the type reported in this paper. It is hoped that these results will be published at some future date. The

author's purpose in this paper has been solely to describe the new methods evolved for carrying out these determinations and the results quoted must be taken only as illustrating these methods. It is hoped that the procedure described will be found as useful to other investigators in this field as they have been to the writer.

ACKNOWLEDGMENTS

The writer's thanks are due to Mr. R. S. Archer and Dr. S. L. Hoyt of the Metallurgical Department of the A. O. Smith Corporation for valuable advice and discussion while carrying out the work described in this paper, and to the Officials of the A. O. Smith Corporation for permission to publish the results.

DISCUSSION

(John Johnston presiding)

J. JOHNSTON,* Kearny, N. J.—This paper describes work, obviously carried out with great care, in which many are interested. At the last meeting of this Division, we passed a resolution endorsing a cooperative investigation, to be carried out under the auspices of the Bureau of Standards, of the several methods now used in various laboratories for the determination of oxygen in steel. That investigation is now actually under way; the several types of material agreed upon as most representative are in the hands of the Bureau of Standards, which is making preliminary analyses of the uniformity of the bars and will soon be ready to send samples to anyone interested in taking part in this comparison of methods. Cooperation has already been promised by several laboratories abroad as well as by practically all of those in this country that have been analyzing steel for oxygen content. I am inclined to think that some of the questions raised by Dr. Reeve's paper can only be definitely answered when we have the results of proper comparative determinations, made by the various methods, on identical samples, such as is contemplated in the cooperative investigation just outlined.

W. H. HATFIELD,† Sheffield, England (written discussion).—The work described in Dr. Reeve's paper strikes me as a vast improvement in the method of analysis of the gas content of metals. Apart from his improvement of the pumping equipment, Dr. Reeve is to be congratulated in his attempt at fractional extractions of the oxygen contents so as to yield some information regarding the relative distribution of the oxygen among the four elements iron, manganese, silicon and aluminum. While this fractional extraction cannot be claimed to give accurate results as regards this distribution, it does provide a fairly reliable guide and will be very useful to the study of the heterogeneity of steel if the method is applied to samples taken from various portions of an ingot.

Unfortunately, the experiments described have been on weld metal, which cannot be compared with results, of which I am familiar, of other methods of oxygen determinations made on samples taken from steel ingots. It would therefore be of considerable interest if Dr. Reeve could analyze by his methods samples taken from some of the ingots examined by the Heterogeneity Committee of the Iron and Steel Institute.

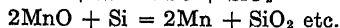
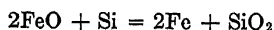
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† The Brown-Firth Research Laboratories.

As regards criticisms of the method, points needing further enlightenment are:

1. An exact estimate of the completeness with which the oxygen from each fraction is extracted.

2. The error introduced by the upsetting of the equilibria:



3. A more complete explanation of the high H_2 values obtained by the fractional extraction as compared with the ordinary fusion.

As regards point 1, figures are quoted in Table 2. The author, however, remarks that "the results were liable to be erratic on repeat experiments," which somewhat detracts from the value of the method, unless these variations are more completely understood. As regards point 2, this is an open question, about which little is known, while point 3 is not too satisfactorily explained.

H. C. VACHER,* Washington, D. C. (written discussion).—A fractional vacuum fusion analysis is an excellent idea and tends to offset the serious disadvantage of the usual vacuum fusion method, which tells nothing of the distribution of the gases in the steel sample. It should be possible to apply the fractional method to any steel where the sum of the fractions is equal to the total amount of gases shown by the usual vacuum fusion method. Manganese oxide and silicon oxide may exist in a variety of combinations in different steels and probably are the most difficult to separate by a fractional procedure common to all steels. For this reason, the practical application of the fractional method might be limited to two temperatures; a low temperature where the greater part of the oxygen evolved would represent oxygen combined as ferrous oxide, manganese oxide, and manganese silicates rich in manganese oxide, and a high temperature where the greater part of the oxygen evolved would represent oxygen combined as silica, alumina and manganese silicates rich in silica.

The author's principal improvement in the apparatus used by the Bureau of Standards for the vacuum fusion method is that the author's apparatus can handle large amounts of gas. However, large amounts of gas are limited to special ferrous materials such as bare wire weld. The Bureau's apparatus is adapted better to materials containing in the range of 0.003 to 0.1 per cent oxygen and 0.003 to 0.02 per cent nitrogen.

The statement that a vacuum fusion analysis requires 8 hr. is not in accord with experience at the Bureau. We have found that if the graphite crucible rests on a beryllia refractory block, the preliminary evacuation period can be shortened to compare favorably with that for the author's specially designed crucible. The time required for a gravimetric analysis also has been shortened by the use of an additional diffusion pump to circulate the gases through the analysis train during the evacuation of the sample. The tubes are ready for weighing very shortly after outgassing of the sample is completed. It is probable that with these minor improvements the total time required by the Bureau's apparatus is less than that required by the author's apparatus. In a sample analysis by the author's apparatus, there is considerable manipulation; such as evacuation with Topley pump, transfer of gases to Orsat apparatus and the numerous volume measurements required by an Orsat apparatus. These manipulations may introduce errors. In the gravimetric method the only serious source of error is in the handling of the weighed absorption tubes.

N. A. ZIEGLER,† East Pittsburgh, Pa. (written discussion).—Of particular value in Dr. Reeve's work is the fractional method developed for the analysis of different

* U. S. Bureau of Standards.

† Westinghouse Research Laboratories.

inclusions and gases in metals. It was known before that the temperatures necessary for complete reduction for different oxides are quite different, but it never was as nicely demonstrated as in the present work.

The results on reduction of powdered oxides are in a good agreement with ours¹⁶ except that the percentages of oxygen yielded, as compared to the amounts of oxide introduced, are somewhat lower than ours, which may be explained by furnace temperatures being considerably lower. In fact, it is surprising that Mr. Reeve gets results as high as given in Table 2 at temperatures as low as 1050° C. for FeO, 1150° C. for MnO, 1300° C. for TiO₂ and 1600° C. for Al₂O₃. In our experiments it was necessary to go to 1600° C. for FeO, and to 1750° C. for the other oxides, to make the reactions at least 90 per cent complete. This difference may be due to the tin added to the charge by Dr. Reeve, which was not done in our work. It is very interesting to note that Dr. Reeve had to add powdered graphite to his oxide samples to bring reactions to completion. This is in perfect agreement with our experience.

The information in regard to the manner and completeness of the extraction of hydrogen and nitrogen from metals is very valuable. It always has been felt that different nitrides may have their properties as widely different as oxides; Dr. Reeve confirms this opinion.

It seems that the time used by Dr. Reeve for degasification of his samples (60 min.) could be reduced, thus reducing the errors entering from the blank correction. In our work¹⁷ 20 min. is sufficient for degasification of a sample exceptionally high in gaseous elements. For the routine work 10 min. suffices.

It is not clear why it is necessary to completely dismantle the furnace after every determination. It seems that if several samples, instead of one, could be held in the water-cooled head C, several analyses could be performed in the same set-up, thus considerably reducing time without sacrificing accuracy.

A. McCANCE, Glasgow, Scotland (written discussion).—In the difficult technique of the methods for determining oxides in steel Dr. Reeve has made a definite advance and the future development of the method that he describes in his paper will be awaited with interest. Based as it is on sound theoretical principles, the method of fractional reduction of the inclusions would appear to offer great hopes of a semi-quantitative solution of the very difficult task of determining the distribution of the oxygen in steel. After all, there has been no great advantage gained from a knowledge of the total oxygen content as yet—and indeed there was no great advantage to be hoped from this knowledge—but every achievement in this direction was welcomed nevertheless, as a step towards a real solution of the problem, which is ever before steelmakers, of making a better quality of steel with a reduced content of nonmetallics. A knowledge of the distribution of the oxygen in the inclusions gives at once, however, a hope that the time is approaching when the content of inclusions and the furnace slag conditions can be definitely correlated, and it is for this reason that I regard Dr. Reeve's work as important.

It is unlikely that the reasons given on page 97 for fearing that the estimated results for FeO will be low where the steel has been deoxidized by silicon or manganese will lead to any error. If equilibrium has been attained at 1600° it is to be remembered that this refers to the liquid condition and that it is improbable that the equilibrium will be affected at all at 1100° C. when the steel is in the solid condition, since change¹⁸

¹⁶ N. A. Ziegler: Reduction of Oxides in the Graphite Vacuum Fusion Method of Analysis for Oxygen. *Min. & Met.* (June, 1933) 260.

¹⁷ N. A. Ziegler: Improved Method for the Analysis of Gaseous Elements in Metals. *Trans. Electrochem. Soc.* (1932) 62, 175.

can only take place by diffusion alone. I think it can be accepted that for all practical purposes the content of FeO found will be exact, or at any rate free from this source of error.

C. H. HERTY, Jr.,* Pittsburgh, Pa.—The method in this paper is to me a very successful application of a principle that has been tried for some time. When we started on the FeO and MnO work, the first paper that came to our attention was by Oberhoffer and Von Kiel, where they tried to differentiate between MnO and FeO by reduction with hydrogen at different temperatures. About three years later we attempted to differentiate between MnS and FeS by hydrogen reduction and we were fairly successful, but not enough so to warrant going ahead with it.

The point that sticks in my mind at the moment is that five or six years ago many people felt that if we could differentiate between the different kinds of oxides and analyze them accurately it would be a long step ahead in the steelmaking game. That, of course, is absolutely correct for certain products. For welding may be 100 per cent correct, but I believe the general tendency now in regard to a large quantity of steel that is produced is to feel that the really important thing is to know not what kind of oxides and how much are present, but the state of aggregation of the oxide. I feel that that is a good deal more important than the total oxygen, even though the total oxygen be split up as so much FeO, so much silica and so much alumina. It is going to be an extremely difficult job to say that we have 0.03 per cent oxygen as alumina, and that is graded into five different fractions as far as size is concerned, but it does seem to me that with this method and others that are being developed we certainly should be able to differentiate between the different oxides present and that the next step is to differentiate between the different sizes of the different oxides; and to me at the moment that is the most important thing about oxide analysis, particularly in view of the intense work that is going on in such lines as aging and hardenability, in which certainly the size of the dispersed particle is extremely important.

A. B. KINZEL,† New York, N. Y.—The precision and general planning of the work by the author of this paper deserve special commendation. The idea as applied is new and the author also deserves credit therefor.

The question of equilibrium in the melt leads to certain thoughts. In the production of the usual killed steel there is residual silicon in the metal at approximately 1600° C. If this silicon is in equilibrium with the iron oxide at this temperature, there will presumably be no further reaction when evolving gas at 1100° C. If there is equilibrium at 1600° C., the distribution of oxygen between alumina, silica, MnO and FeO may be calculated from equilibrium constants and there is no need to make fractional analysis. Fractional analysis is necessary only if the relative contents of the various oxides do not correspond to equilibrium at the pouring temperature. If this equilibrium does not exist, we should expect further reaction on melting even at a lower temperature, such as 1100°, whereby any free aluminum or silicon would react with the FeO. This would give fractional analysis values that would only be apparent and that would not represent the true condition. Accordingly, if the oxides are not in equilibrium when pouring, there is difficulty in getting a true figure from the fractional analysis, and if they are in equilibrium when pouring, there is no need for a fractional analysis. Obviously, even though there is a small reaction at the lower temperature and the fractional analysis is not accurate, it may still be very worth while, in that the relative order of magnitudes may be measured; that is, the analysis may give a large

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† Metallurgist, Union Carbide and Carbon Research Laboratories.

part of the original FeO as such. In this method we have another tool for use in studying the oxide problem. Like many other tools that we have had to date, it seems to have certain limitations, and we cannot judge it without further experience. The author is to be congratulated on conceiving and studying this approach to the problem.

J. JOHNSTON.—We have been working for two or three years on an improved method of reduction by hydrogen as a means of analyzing steel for oxygen. In this work we very soon discovered that results are erroneous if iron is in contact with silica at 1000° to 1100° C. in presence of hydrogen, which under these circumstances reduces silica; but it took a longer time to recognize the unexpected fact that hydrogen reduces some silica at this temperature in presence even of iron vapor, though in the blank experiment the amount of such reduction is zero. This difficulty was surmounted by the use of a high-frequency furnace, which heats the suspended sample without bringing the enclosing silica tube to a temperature at which this reaction is appreciable. The details of this modified method, with some of the results obtained, we hope to submit for publication soon. Here it suffices to say that, the steel being kept at about 1100° C., we seem to get in about an hour all of the oxygen that will come off at that temperature; and that we interpret this oxygen as representing FeO, possibly MnO to some extent, and probably some proportion of the silica or silicate, the proportion depending upon the fineness of grain of the inclusions.

L. REEVE.—In reply to Dr. Vacher, I want to say that while the description of the procedure of evacuation and so on sounds very laborious, as an actual fact it takes up, mathematically speaking, no time at all. That is to say, I spend no extra time in collecting my gases out of the equipment apart from the time required, in any case, to get those gases off the melt. If I am in a hurry I pump off the gases as soon as they come off, and collect them in a test tube. That takes no additional time. Gas analysis takes about $\frac{1}{2}$ hr. per sample on an Orsat apparatus.

With regard to the statement, too, that the time mentioned, 8 hr., is not correct, I presume that means it is not correct at the present moment; but at the time we started doing this work, late in 1931, Dr. Thompson, of the Bureau of Standards, told us he took about 9 hr. to carry out a determination.

I think the main point of importance has been raised by Dr. McCance and Dr. Kinzel; that is, with regard to the possible displacement of equilibrium. That worried me for a long time. It struck me as fundamentally perhaps the weakest point in the method, but just before this paper was written, we carried out a number of determinations on a piece of gray iron, which gave a great deal of valuable information, and, while not absolutely disproving the possibility that displacement of equilibrium may take place to a slight extent, indicated that the actual amount of displacement was very much smaller than I feared. We had a gray iron that was known to be pretty poor as far as physical properties were concerned, and yet was known to contain high carbon, of course, and high silicon. Its analysis is given in footnote 11. With that amount of silicon and certainly with that amount of carbon, we did not expect much oxygen. When we came to analyze the sample by the fractional method we found 0.047 per cent of oxygen as FeO plus MnO. Those who are familiar with the subject will agree that this is a considerable amount. A considerable part of this oxygen, I do not recall the exact amount, was FeO; the O_2 as SiO_2 averaged only 0.007 per cent and the microexamination of the specimen confirmed the fact that there was a slight amount of siliceous material there. The surprising thing is that with 1.7 per cent silicon it was possible to have a sample that apparently was not deoxidized in the usual sense of the term; that is to say, at the pouring temperature of this gray iron, the silicon had not reacted with the iron oxide present. The iron, of course, may

have become oxidized in the mold. But, here again, in the fractional method of analysis I remelted the specimen at a temperature of 1050°C . (in the presence of tin) and again the silicon apparently did not react to any more than the extent of 0.007 per cent, and possibly less, so it looks as though the possibility of deoxidation by silicon during the actual determination is certainly not going to be as bad as I thought it might be.

I think there was some misunderstanding by Dr. McCance with regard to the state of aggregation of my material. I am working with a liquid even at 1050°C . He refers to my material as solid.

Dr. Johnston spoke of the reduction of silica by hydrogen. It certainly strikes me as a remarkably low temperature. I did not find that with carbon; I certainly had no appreciable reduction at 1100°C . The point Dr. Johnston raised about the fineness of the grain certainly should be borne in mind.

I agree with Dr. Herty that the state of aggregation is as important to the physical properties as the amount of material.

T. SWINDEN,* Stocksbridge, England (written discussion).—The improvements Dr. Reeve has made have put the vacuum fusion method on a really workmanlike basis, and this is a very important feature. It will encourage other people to develop this method which, after all, is, I think, generally recognized as the most reliable method for the determination of total oxygen in steel.

The work Dr. Reeve has done on the determination of FeO and MnO , SiO_2 and Al_2O_3 , by fractional extraction is extremely interesting. At the same time, as he points out, the interaction of the oxides when heated will, I am afraid, render absolute figures on this basis somewhat problematical. Nevertheless, it is an extremely useful suggestion and one that we intend to follow up further in our own laboratory when we have the opportunity of installing the requisite apparatus. Altogether, Dr. Reeve's paper must be regarded as a most useful and constructive contribution to the subject and one that will be referred to by all workers in this field.

C. BENEDICKS† and G. ERICSON,‡ Stockholm, Sweden (written discussion).—We have studied the paper with much interest; we especially appreciate the increase in accuracy represented by but one single specimen being analyzed each time, in spite of the loss of time resulting.

As for the reliability of the method, the writers, after a careful experimental analysis of the vacuum exhaustion method,¹³ have satisfied themselves that a quantitative working is possible to reach, but only under some special precautions. The most important point is to avoid the sputtering of the oxide specimen. As a matter of fact, the reduction of the oxides of iron, manganese and silicon takes place in a very energetic way—nearly implying explosions—which causes the oxide partly to be blown out of the crucible, with great losses of oxygen. On account of this, the writers found it necessary for an accurate working with oxide powder to let the carbon monoxide formed pass through a glowing layer of graphite powder, kept in the upper part of the crucible. It was not easy to understand that without such a precaution an output of 100 per cent was now sometimes obtained in the case of SiO_2 ; probably the considerable height of the crucible used by the author (6 in.), as compared with that of the present writers (4 in.), might be the reason of the sputtering causing lower losses.

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† Director, Metallographic Institute of Stockholm.

‡ Metallographic Institute of Stockholm.

¹³ G. Ericson and C. Benedicks: *Jernkontorets Ann.* (1931) **86**, 549. Abstract: *Stahl u. Eisen* (1932) **52**, 565.

The principal objection against the apparatus as described was the use of a radiation shield (the sillimanite protection tube). This being quite close to the glowing graphite, a reaction can hardly be avoided. The use of such an oxide tube, according to our opinion, is the main reason for the high blank values obtained. We found it absolutely necessary to avoid such tubes. As a matter of fact, with modern possibilities a radiation shield is not required for obtaining high temperatures.

It should be remarked in this connection that no description has been given of the manner in which the corrections have been made for the influence of the blank value. The influence of this correction is prominent, especially for the hydrogen content. According to experience gained by the present writers, the blank gas as a rule contains about 85 per cent hydrogen. Hence the influence of a high blank value is a considerable one for hydrogen.

To judge from Fig. 1, the leads used by the author are rather long and narrow, which considerably increases the difficulty of obtaining a satisfactory vacuum. Besides, the presence of stopcocks in the high-vacuum leads also increases this difficulty. They should be entirely avoided.

A loading device of simpler construction than the one used, permitting the storing of a number of samples, is described in the paper of the present writers.

The reduction temperatures indicated in the paper tally fairly well with those found in the work of the present writers. They hope that these remarks may be of some value for the continued work. An increase in the accuracy of the method is indispensable in order to get reliable results for steel samples with very low oxygen values.

L. REEVE (written discussion).—The method described is, of course, equally applicable to ordinary steel samples. The differences as compared with weld metal are purely quantitative. The writer has analyzed a number of steel samples, both rimmed and killed, by the fractional method. The only changes he would like to introduce are in the direction of increasing the accuracy of the method by using larger steel samples and by reducing the value of the blank corrections. The latter incidentally are almost negligible at temperatures up to about 1400° C., but become relatively more marked at the temperature of the third fraction. Both these improvements are perfectly feasible. With regard to the other points raised by Dr. Hatfield:

1. As regards the completeness with which the oxygen from each fraction is extracted. It has been pointed out in the experiments on reduction of powdered oxides and silicates, described on pages 90 to 92, that it is difficult to duplicate the reduction of inclusions in a steel sample by means of such experiments. The fact that results are erratic has been pointed out by other experimenters, in particular by Diergarten and by Benedicks. The latter refers to this difficulty in his written discussion.

The writer believes that conditions are far more favorable to the reduction of inclusions already present in a steel sample than when powdered oxides are dropped on to the surface of a melt. In the latter case, they are liable to agglomerate into a "clot" (p. 91), and to float unreduced on the surface. When this tendency is overcome, considerably better results are obtained.

Benedicks suggests that inclusions may be blown explosively out of the crucible, and suggests a guard of glowing graphite above the melt. The writer has occasionally introduced this guard by the simple procedure of dropping one gram of graphite powder into the crucible before starting an experiment. It certainly appeared to be helpful. (See p. 91.)

Ziegler refers to his experiments on powdered oxides, in which apparently he was able to obtain 100 per cent yields even with alumina, by adding powdered graphite to his oxides.

In general, the author is of opinion that the general conclusion from these experiments is that the completeness of reduction of most oxides (with the possible exception of alumina) is at least 90 per cent.

2. With regard to the possible error introduced by the upsetting of equilibria; the writer dealt with this matter in his oral reply (p. 106). It would seem that the writer's fears with regard to displacement of equilibrium are probably groundless, and even if it were possible to have a steel containing iron oxide in the presence of free silicon, or aluminum (rather doubtful in the case of a steel melted at $1600^{\circ}\text{C}.$, although apparently possible in the case of a gray iron), such iron oxide would not be acted upon by the free silicon under the conditions of the analysis.

3. With regard to the higher H_2 values given by the fractional method, the writer must confess that he gives the results for what they are worth. Tin may have an effect on hydrogen solubility either by decreasing it in the melt or by affecting the surface tension of the melt, as suggested by recent investigators in this field. Alternatively, the longer time taken by a fractional determination may have something to do with the greater completeness of hydrogen removal.

The writer appreciates Dr. Vacher's suggestion that possibly two temperatures might be sufficient in practice for carrying out the fractional method, but he cannot agree entirely with the subdivision suggested, particularly with regard to the reduction of manganese silicates. However, some such division at, say, $1200^{\circ}\text{C}.$ to include FeO and MnO , and at $1570^{\circ}\text{C}.$ or higher to include SiO_2 and Al_2O_3 , might be useful in practice.

The writer's own impression is that the amount of FeO apart from the MnO is often the important factor in determining physical qualities of steel—or at least, of weld metal.

With regard to the time taken for analysis, a "total oxygen" determination can be carried out in about 3 hr., and a fractional in about 5 hr. Under certain conditions, these times may be reduced. The author has sometimes used a head containing multiple samples (up to six), in which case the total time per determination is reduced considerably. There are, however, objections to this practice (such as the piling up of manganese), which have been pointed out by the Bureau of Standards and by German investigators, and for the most accurate work, one determination at a time is advisable. Dr. Bonedicks has overcome some of the difficulties connected with heads carrying multiple samples, and for routine work the procedure may perhaps be sufficiently accurate. It certainly reduces the time for a single determination when total oxygens are being considered. The time saved would not be relatively so marked in the fractional determinations.

The procedure described for handling the equipment is rather like a description of how to handle an Orsat gas analysis apparatus—very much simpler in practice than in print. As pointed out on page 106, the gases may be collected immediately as they come off and no appreciable additional time is required for this purpose. On the whole, the writer thinks it more convenient to handle 1 c.c. of hydrogen as a gas than to weigh it as (approx.) 0.0008 gram of water. No doubt, with practice, equal accuracy is possible by both methods.

The writer is familiar with Mr. Ziegler's excellent work on the reduction of powdered oxides. The presence of metallic tin in the writer's experiments would, of course, give a molten medium in which reactions could take place even at relatively low temperatures. The use of powdered graphite is referred to. It should perhaps be pointed out, that the writer placed his graphite in the crucible at the beginning of a test, and that this graphite powder would be pre-evacuated during the evacuation of the crucible. Mr. Ziegler mixed the graphite directly with his oxide, and dropped the mixture into his evacuated furnace. This no doubt helped to give better percentage yields, but there is some possibility of a little gas being present in the powdered graphite.

The time given for the complete degasification of a sample errs deliberately on the high side; in many cases, 30 min. is sufficient. The still shorter time mentioned by Mr. Ziegler is no doubt due to the higher top temperature at which he works.

The writer is now (April, 1934) associated with the United Steel Companies, and the specific points raised by Dr. Swinden will no doubt be investigated at the first opportunity.

The extremely important aspect of the inclusion problem raised by Dr. Herty lies outside the special field dealt with by the writer. No doubt the size of inclusion plays an important part in determining the quality of a steel. There has not been sufficient agreement in the past on suitable methods for determining accurately the type of inclusion to warrant reliable deductions as to their importance. The writer would feel very happy if he knew that he had helped to solve this specific problem. The future will indicate its relative importance.

The writer is pleased to note that Dr. Benedicks and Mr. Ericson have found that in principle the method may be regarded as quantitative, subject to the type of precaution mentioned by them.

The point regarding the height of the crucible being helpful is probably correct.

With regard to the employment of a sillimanite radiation screen, the writer has never found any serious difficulty as regards evacuation with the suspended type of crucible.

The blanks at temperatures up to 1400° C. are almost negligible, and even at 1570° C. are not serious. The writer, however, agrees that it is possible to reduce these blanks still further, and that the removal of the screen might be useful. A description of the method by which the blanks are determined is given on pages 87 and 93.

The lead from the furnace to the mercury diffusion pump is made extra wide (about 17 mm. internal diameter). The photograph does not show this very clearly, although careful examination will indicate that this tube is wider than in the rest of the equipment. An extra large stopcock (1 cm. bore) is also used in this portion.

The last paragraph of Dr. Benedicks' discussion is of particular interest to the writer, because this is the first independent check of the reduction temperatures he has employed.

Determination of Oxygen in Alloy Steels and Its Effect upon Tube Piercing

By NEWELL HAMILTON,* BEAVER FALLS, PA.

(New York Meeting, February, 1934)

SOME years ago, in the manufacture of seamless tubing from an alloy steel containing 0.07 per cent maximum carbon, 18 per cent chromium and 8 per cent nickel, at the plant of The Babcock & Wilcox Tube Co., a peculiar type of piercing defect was noticed. This defect was definitely associated with certain heats of the alloy and was independent of any of the variables of mill operation and billet-heating condition. A thorough analysis of the defective material yielded but one clue to the reason for its abnormal behavior in piercing and that was its oxygen content as determined by the vacuum fusion method.

The oxygen content of the defective 18-8 alloy was found to be from two to three times that of the material that had pierced satisfactorily, and this incited an active interest in the vacuum fusion method for the analysis of alloy steels. After a critical survey of the literature on this subject, and considerable experimentation, an apparatus and technique were evolved that gave a fairly rapid, simple and reliable method of analysis. Samples selected from six years of tube production of 18-8 and other corrosion-resistant alloys were analyzed by this method. This paper describes the procedure and gives a correlation of the oxygen, hydrogen and nitrogen contents of a number of alloy steel samples representative of good and bad tube-piercing quality.

THE APPARATUS

Basically the apparatus used in this work was that of Jordan and Eckman,¹ employing a high-frequency induction furnace and the gravimetric method of analyzing the evolved gases, nitrogen being excluded from the determination. In addition, a magazine-type cap and a large-

Manuscript received at the office of the Institute Nov. 29, 1933.

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¹ L. Jordan and J. R. Eckman: The Determination of Oxygen and Hydrogen in Metals by Fusion in Vacuum. U. S. Bur. Stds. *Sci. Paper* 514 (1925).

capacity mercury diffusion pump were used, as suggested by Hessenbruch and Oberhoffer.²

The apparatus (Fig. 1) consists of a high-frequency induction furnace, a McLeod gage of standard make with a range from 0 to 250 microns, a four-stage all-metal mercury diffusion pump, an analytical train and a small rotary vacuum pump. All of the glass tubing and glassware in the apparatus is Pyrex, to facilitate repair work, and the stopcocks

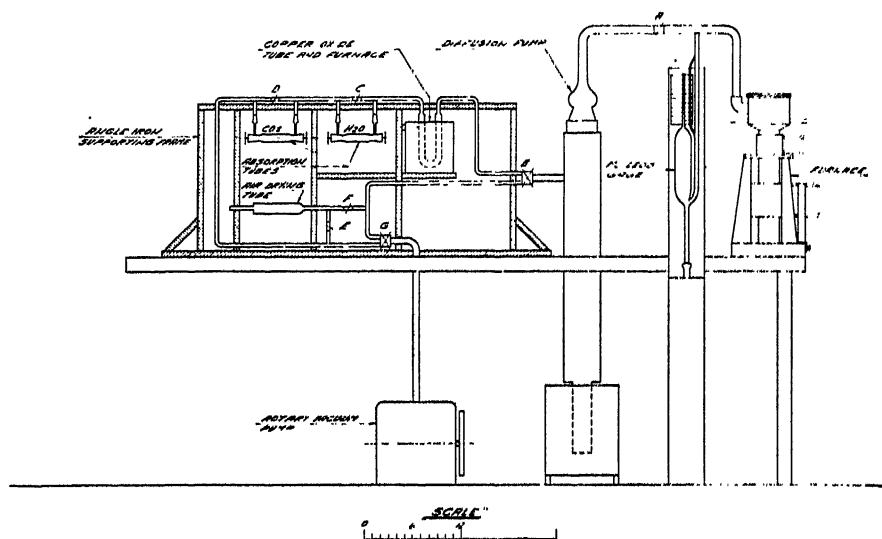


FIG. 1.—DIAGRAM OF APPARATUS USED IN DETERMINATION OF ALLOY STEELS.

are especially selected with large barrels ground carefully for high-vacuum work. The analytical train is mounted upon an angle-iron frame and consists of a copper oxide U-tube enclosed in a small electric resistance furnace and two removable absorption tubes of the type described by Vacher and Jordan,³ filled with suitable absorbents. The glass tubing connecting the furnace cap and the diffusion pump is of large diameter in order that the transfer of gases from the furnace may be rapid.

The details of the cap and furnace construction are shown in Fig. 2. The cap, sample magazine and outlet elbow were all machined from wrought 18-8 alloy but might have been made from any nonmagnetic alloy, such as brass. The cap proper was machined from one solid piece

² W. Hessenbruch and P. Oberhoffer: An Improved Method for the Rapid Determination of Gases in Metals, Especially Oxygen in Steel. *Archiv f. d. Eisenhüttenwesen* (1928) 1, 583-600.

³ H. C. Vacher and L. Jordan: The Determination of Oxygen and Nitrogen in Irons and Steels by the Vacuum Fusion Method. *U. S. Bur. Stds. Jnl. of Research* (1931) 7.

in such a manner that only one soldered joint was actually subjected to the vacuum, that being where the outlet elbow is attached. The sample magazine contains six compartments symmetrically placed around the funnel. Across the bottom of each compartment in a radial direction is a small nickel pin, which retains the sample in the magazine. Withdrawing this pin by means of an electromagnet held on the outside of the cap allows the sample to fall through the funnel into the crucible. By this arrangement it is possible to drop any one of the six samples into the crucible at any time without interfering in any way with the vacuum in the furnace.

A circular piece of plate glass is sealed over the top of the cap with wax, permitting observation of the samples and crucible at all times. Removal of this glass plate allows free access to the loading magazine and the furnace and permits the necessary replacements to be made by breaking only one vacuum-tight seal.

The cap is sealed on the top of the silica tube with wax; this seal being more or less permanent and protected from the heat of the crucible by a water jacket around the silica tube and above the high-frequency coil. This water jacket consists of a coil of copper tubing firmly cemented to the silica tube with a sodium silicate-metallic zinc cement that has fairly good thermal conductivity.

The graphite crucible is supported upon a graphite pedestal which in turn rests upon granular magnesite in the bottom of the silica tube a safe distance from the field of the high-frequency coil. This construction was suggested by the design of furnace used by Von Seth.⁴ A sillimanite radiation shield surrounds the crucible and prevents an undue amount of radiant heat from reaching the silica tube. By this construction all possible contacts between hot graphite and refractory are avoided and gas evolution as a result of the reduction of refractories by the graphite is eliminated.

The high-frequency coil was actuated by a Northrup generator of 35 kva. capacity. With this power source and the coils available it was possible to obtain temperatures as high as 2000° C. The temperature in the crucible during degasification and the metal temperature during parts of the analysis were measured continuously by means of a radiation pyrometer sighted down into the crucible through the glass plate on the top of the cap.

THE METHOD

The operation of the apparatus does not differ greatly from the original method of vacuum fusion analysis described by Jordan and

⁴ R. Von Seth: The Determination of Oxygen in Iron by Melting in Vacuum. *Jernkontorets Ann.* (1928) 83, 113-150.

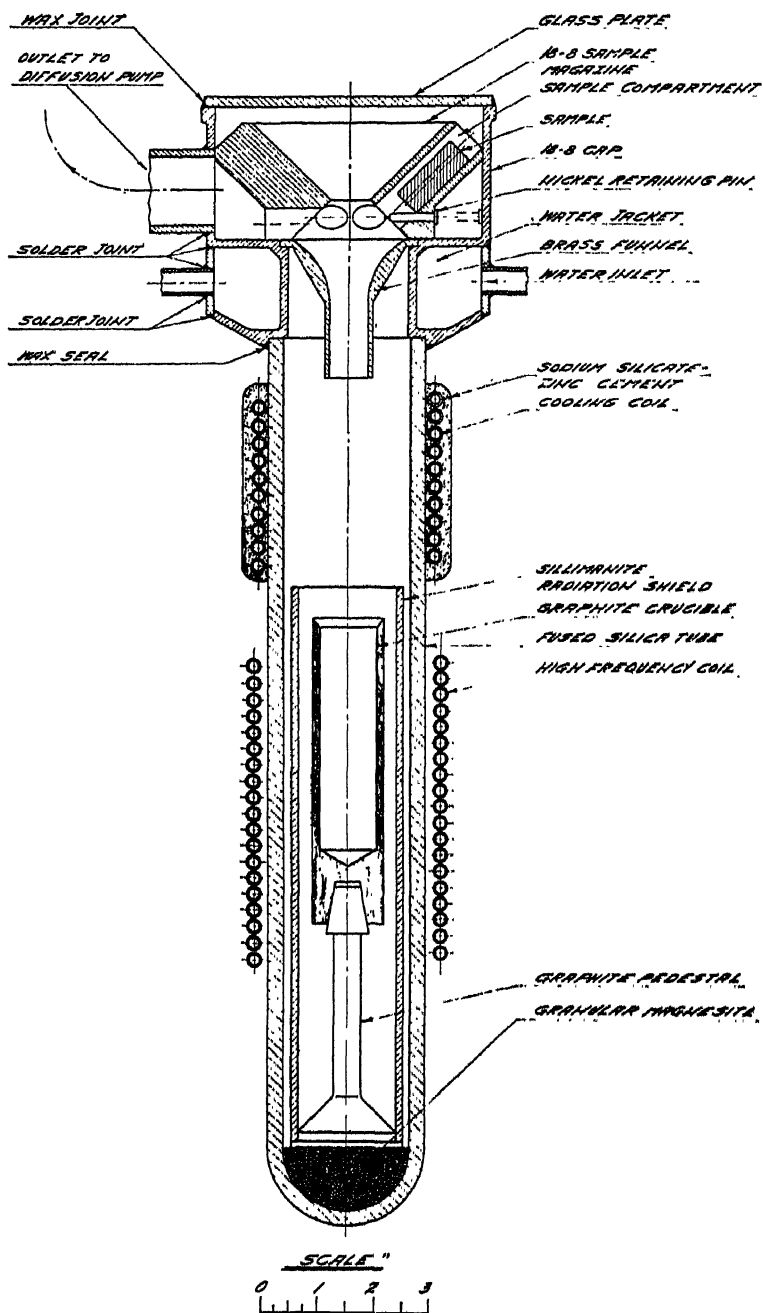


FIG 2.—DETAILS OF CAP AND FURNACE CONSTRUCTION.

Eckman. The various modifications of their original apparatus have brought about some changes in the technique of the analysis which may be briefly summarized as follows:

1. Higher temperatures of crucible and sample degasification tending toward greater assurance of a complete reduction of the oxides in the sample.
2. Lower pressures and greater evacuation rates during an analysis, permitting more rapid determinations.
3. A cap and furnace construction that permits the analysis of six consecutive samples and eliminates the blank correction by minimizing the gas evolution from refractories.

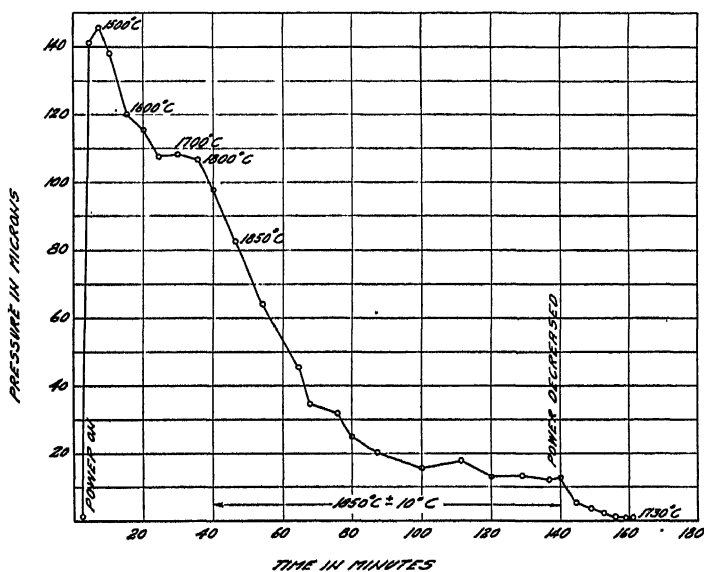


FIG. 3.—CRUCIBLE DEGASIFICATION.

Fig. 3 shows a record of a typical crucible degasification, time being plotted against pressure with the temperature indicated. This operation requires from $1\frac{1}{2}$ to 5 hr., depending, presumably, upon the amounts of impurities in the graphite. The blank for the apparatus, after degasification to a pressure of one micron at 1700° to 1725° C., is unweighable and is therefore less than 0.00015 per cent oxygen and 0.00005 per cent hydrogen. Degasification pressures of 3 microns were found to yield blanks that were just barely weighable.

The filling, cleaning and weighing of the absorption tubes is done with the utmost care. One filling usually suffices for a series of six determinations. The tubes are subjected to triple washings with ether and the weighing is done upon a Troemner analytical balance of high sensitivity,

the smallest weighing division of which is 0.00005 grams. From experience it was found that the errors in weighing were within 0.0001 grams.

The earlier forms of the apparatus had another set of absorption tubes placed ahead of the copper oxide tube. This was found to be unnecessary because the amounts of carbon dioxide and water vapor evolved as such from a sample during analysis were negligible and did not affect the accuracy of the method when absorbed and calculated as carbon monoxide and hydrogen.

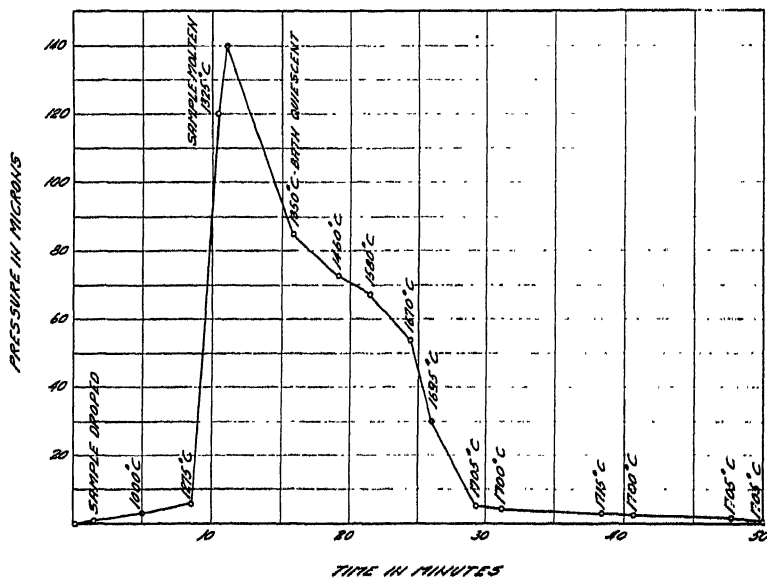


FIG. 4.—DEGASIFICATION OF SAMPLE OF 18 PER CENT CHROMIUM, 8 PER CENT NICKEL STEEL.

Weight of sample, 22.242 grams; oxygen, 0.0062 per cent; hydrogen, 0.009 per cent.

Fig. 4 shows a record of a typical 18-8 sample degasification, plotting time against pressure with the temperature indicated. The time required for this operation varies with the sample weight and the amount and combination of the oxygen and may be from 20 min. to 1 hr. and 30 minutes.

The application of this method to the analysis of alloy steels, particularly 18-8, required an investigation of the reproducibility of the method and the effect of temperature of sample degasification. This was accomplished by the selection of a "standard" sample of this material and the analysis of a number of these samples at various degasification temperatures both in empty degasified crucibles and consecutively in the same crucible. The results of a number of these analyses are given in Table 1.

TABLE 1.—*Analyses of Standard Samples of Steel Containing 18 Per Cent Chromium and 8 Per Cent Nickel*

Temperature of Degasification, Deg. C.	Gases, Per Cent		Temperature of Degasification, Deg. C.	Gases, Per Cent	
	Oxygen	Hydrogen		Oxygen	Hydrogen
1500	0.0090	0.0016	1675	0.0128	0.0016
1525	0.0112	0.0026	1675	0.0123	0.0026
1575	0.0104	0.0008	1700	0.0130	0.0030
1600	0.0106	0.0008	1700	0.0131	0.0020
1625	0.0108	0.0008	1700	0.0123	0.0030
1625	0.0121	0.0017	1725	0.0129	0.0020
1650	0.0113	nil	1750	0.0130	0.0030
1650	0.0124	0.0016	1775	0.0127	0.0028
1675	0.0103	0.0007			

The values for oxygen are almost uniform above 1675° C., and below this temperature are low and erratic, therefore the temperature range for degasification was set at 1700° to 1725° C.

The extensive work of almost all other investigators has indicated that complete reduction of even the most refractory oxides may be accomplished by the vacuum fusion method, providing high enough temperatures are used. As the present investigation was concerned with a comparison of various heats of the same types of steel, more attention was paid to the reproducibility of the method than to an investigation of the completeness of reduction of the various oxides. During the course of the work it was found that certain samples known to contain aluminum, zirconium, titanium, etc., required longer degasification periods. A great many samples were run in duplicate and triplicate with results indicating that the method yielded results reproducible within 0.0005 per cent oxygen.

One source of error in checking results was traced to sampling, as in general higher values for oxygen were obtained on samples cut from the core of a billet than on those cut from near the outside. In some cases the difference between these two values was as high as 50 per cent and for this reason care was taken in cutting the sample to see that representative amounts of core and rim material were included.

Early in the work it was found that any attempt to include nitrogen in the gases determined in the vacuum fusion analysis made the apparatus and technique more complicated. Except in rare instances, such as 18-8 alloys containing titanium or other alloy ingredients forming insoluble nitrides, the modified Allen distillation method as described by Jordan and Swindells⁵ gave satisfactory results.

⁵ L. Jordan and F. E. Swindells: *Gases in Metals, I—The Determination of Combined Nitrogen in Iron and Steel and the Change in Form of Nitrogen by Heat Treatment*. U. S. Bur. Stds. *Sci. Paper* 457 (1922) 18.

RESULTS

In order to investigate the effect of oxygen on the tube piercing of 18-8 alloy, a number of heats were selected from the mill production of this alloy. In each case the heats selected were either good or bad and nothing was left in doubt concerning the mill variables that might possibly have affected the piercing. As some six years of tube-production records of the alloy were available it was possible to select only heats of which the histories were definitely known. In all cases the bad material had been run along with some good material in order to make the comparison more exact.

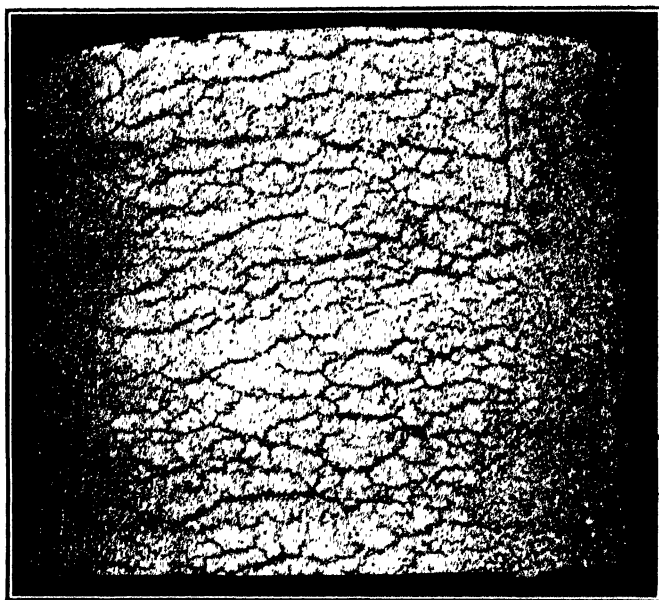


FIG. 5.—HEAVY CHECKING IN A PIERCED HOLLOW OF 18-8 ALLOY.

The defect that occurred in the heats that were selected was called "outside checking," and consisted of outside transverse cracks originating in the piercing mill. After plug rolling these cracks opened and varied in depth from a few thousandths of an inch to ruptures entirely through the wall of a heavy-walled tube. Fig. 5 shows a case of heavy checking of this type in a pierced hollow of 18-8 alloy. The defect has been analyzed as a lack of high-temperature ductility in the metal and has been in all cases directly traceable to a particular heat of steel.

The samples selected for vacuum fusion analysis were cut from either billets or tubes, so that the same ratio of core and rim was maintained in all cases. Nitrogen determinations were made on these heats by the distillation method. The usual chemistry of these heats was well within

the commercial range for this alloy and absolutely no correlation existed between the outside checking and the carbon, manganese, sulfur, phosphorus, silicon, chromium, nickel or iron contents of the heats.

Table 2 gives the oxygen, hydrogen and nitrogen contents of these heats, and from these results it may be seen that the oxygen contents of the heats exhibiting the checking are from two to three times the values obtained on good material. Likewise, the maximum and minimum oxygen values for these two classifications do not overlap and the degree of checking is roughly proportional to the oxygen content of any one heat. The correlation of hydrogen and nitrogen contents and outside surface checking is not nearly so conclusive. The variation in hydrogen between good and bad materials might be regarded as within the error of the method, and it should be noted that several of the heats showing checking are below the average for good heats in both hydrogen and nitrogen content.

Recently a number of heats of an alloy steel containing 5 per cent chromium, 0.50 per cent molybdenum and 0.16 per cent carbon maximum developed a bad surface condition, which apparently had originated in the piercing mill. The final form of the defect was more in a longitudinal direction than in a transverse direction but it had a close resemblance to the external checking that had occurred on the 18-8. A number of these heats, as well as some that had processed satisfactorily, were analyzed by the vacuum fusion method, with the results shown in Table 3, which show that practically the same difference exists between the oxygen values of the good heats and those exhibiting the outside checking, as in the 18-8 results in Table 2. The values also are of the same magnitude.

All of the alloy steels represented in this investigation were made by the basic electric process in 6-ton to 12-ton heats. The 18-8 heats were processed into tube rounds and then rough-turned to eliminate surface defects, while the 5 per cent chromium, 0.50 per cent molybdenum heats were rolled into tube rounds after chipping in the bloom and in some cases chipping in the round but with no rough turning. Both alloys represent an excellent quality of steel, and the tube billets were carefully inspected before rolling into tubes. It is highly improbable that any surface defects existed on the tube rounds that could have contributed to the checking that was present on the finished tubes.

DISCUSSION OF RESULTS

The results of this investigation indicate that the total oxygen content of two highly alloyed steels bears a direct relationship to the elevated temperature ductility of these steels as determined by the seamless tube piercing. Any theoretical consideration of this problem brings up the question of the manner of combination of oxygen in these steels that

TABLE 2.—*Gases in Alloy Steel Containing 18 Per Cent Chromium, 8 Per Cent Nickel, 0.07 Per Cent Maximum Carbon*

Sample No.	Condition	Gases, Per Cent		
		Oxygen	Hydrogen	Nitrogen
A-1	Good	0.0065	0.0004	0.025
A-2	Good	0.0055	0.0010	0.023
A-3	Good	0.0060	0.0012	0.025
A-4	Good	0.0061	0.0009	0.020
A-5	Good	0.0069	0.0010	0.021
A-6	Good	0.0087	0.0011	
B-1	Good	0.0064	0.0006	0.035
C-1	Good	0.0070	0.0010	
C-2	Good	0.0066	0.0010	
D-1	Good	0.0062	0.0006	
D-2	Good	0.0085	0.0014	
D-3	Good	0.0060	0.0020	
D-4	Good	0.0059	0.0010	
D-13	Good	0.0055	0.0018	
A-11	Good	0.0075	0.0009	0.0188
A-12	Good	0.0060	0.0008	0.0197
	Average	0.00658	0.00104	0.0234
	Maximum	0.0087	0.0020	0.035
	Minimum	0.0055	0.0004	0.0188
E-1	Very heavy checking outside	0.0376	0.0008	0.113
A-9	Heavy checking outside	0.0190	0.0011	0.024
D-9	Heavy checking outside	0.0207	0.0006	0.032
D-10	Heavy checking outside	0.0161	0.0012	0.025
D-11	Heavy checking outside	0.0182	0.0012	0.026
C-6	Heavy checking outside	0.0220	0.0039	
D-12	Checking outside	0.0150	0.0005	0.037
C-9	Checking outside	0.0146	0.0009	
A-10	Light checking outside	0.0127	0.0015	0.022
C-7	Light checking outside	0.0106	0.0012	
C-8	Light checking outside	0.0137	0.0024	
	Average	0.0182	0.00136	0.029
	Maximum	0.0376	0.0039	0.113
	Minimum	0.0106	0.0008	0.022

causes this change in their ductility. Both of the alloys investigated contain appreciable amounts of chromium, and, owing to the great activity of this element, it is probable that the oxygen present is in combination with it. The amounts of inclusions present in these steels at room temperature are not excessive and could not possibly affect the workability of the steel if they were to remain unchanged when heated to the temperatures required for piercing, which are from 2150° to

TABLE 3.—*Gases in Alloy Steel Containing 5 Per Cent Chromium, 0.50 Per Cent Molybdenum*

Sample No.	Condition	Gases, Per Cent		
		Oxygen	Hydrogen	Nitrogen
5CM-B1	Good, no steel loss	0.0069	0.00091	0.0224
5CM-B2	Good, no steel loss	0.0065	0.00069	0.0190
5CM-B3	Good, no steel loss	0.0073	0.00090	0.0238
5CM-B4	Good, no steel loss	0.0078	0.00070	0.0408
5CM-C1	Good, no steel loss	0.0059	0.00140	0.0084
5CM-A1	Good, no steel loss	0.0064	0.00062	0.0358
5CM-A2	Good, no steel loss	0.0060	0.00079	0.0239
5CM-A3	Good, no steel loss	0.0069	0.00097	0.0145
5CM-C2	Good, no steel loss	0.0079	0.00260	0.0126
Average	Good, no steel loss	0.00684	0.00106	0.0223
Maximum	Good, no steel loss	0.0079	0.00260	0.0408
Minimum	Good, no steel loss	0.0059	0.00069	0.0084
5CM-B5	Bad, outside checking	0.0197	0.00098	0.0252
5CM-C3	Bad, outside checking	0.0130	0.00076	0.0187
5CM-C4	Bad, outside checking	0.0173	0.00170	0.0193
Average	Bad, outside checking	0.0166	0.00114	0.0210
Maximum	Bad, outside checking	0.0197	0.00170	0.0252
Minimum	Bad, outside checking	0.0130	0.00098	0.0187

2350° F. (1177° to 1288° C.). This suggests the formation of an oxygen-bearing constituent at elevated temperatures, which would have physical properties differing from the alloy matrix at these temperatures and would be of sufficient volume to cause the pronounced effect upon the elevated-temperature ductility of the alloy that has been noted. Efforts to prove the existence of such a constituent by microscopic examination at room temperature have as yet been unsuccessful.

That some combination of oxygen and chromium is responsible for the abnormal behavior of these steels at elevated temperatures is indicated by the fact that heats of 18-8 alloy that have been subjected to ladle deoxidization with aluminum or zirconium have been successfully pierced even though their total oxygen content has been above the maximum for good piercing quality. This is explained by the supposition that the oxygen in these heats has been "fixed" to a more stable form by combination with aluminum or zirconium so that it does not affect the elevated temperature ductility. Such "fixing" of the oxygen content of a heat of 18-8 is not a satisfactory solution to this problem, for it has been found that the resulting inclusions seriously interfere with the working of the alloy in other ways, to form numerous splits and tears in hot

working that become exaggerated in cold drawing. The fact remains that oxygen in 18-8 and other high-chromium alloys, regardless of its combination, is detrimental to the manufacture of tubes and all efforts should be made to keep it at a minimum. It is realized that this minimum is low (less than 0.01 per cent oxygen) but experience has shown that many thousands of tons of these materials have been made that have contained less than this minimum of oxygen.

ACKNOWLEDGMENT

The author wishes to express his appreciation to the officials of The Babcock & Wilcox Tube Co. for permission to publish the material contained in this paper. Special credit is deserved by W. Spencer Lloyd for the work on the development and operation of the vacuum fusion apparatus. The helpful suggestions of H. D. Newell and the aid of James F. Brett in selecting the samples for analysis are acknowledged. Credit is due Homer N. Austin and Theodore R. Polhemus for the nitrogen determinations.

DISCUSSION

(Jerome Strauss presiding)

H. C. VACHER,* Washington, D. C. (written discussion).—This is one of the first papers to show that oxygen analyses can be correlated directly with plant difficulties. It should act as an incentive to increase the application of the vacuum fusion method and to stimulate research on the behavior of inclusions in steel.

Mr. Hamilton stated that he was primarily interested in obtaining reproducible values for the oxygen content of 18-8 steels. However, his procedure and data are interesting also from the point of view of accuracy. He infers that the same value for an 18-8 steel can be obtained from an empty crucible as from a crucible containing the residue of a previous analysis. It has been shown¹⁹ that a difference between the first and successive determinations was obtained if the material contained manganese and that the difference increased as the manganese content increased. For material containing approximately 0.4 per cent manganese, the amount usually found in low-carbon 18-8 steels, the difference was about 0.002 per cent. The fact that Mr. Hamilton's data show no difference when the same material is analyzed in an empty crucible and when analyzed in a crucible containing the residue of a previous analysis indicates that manganese is not causing an error in the values obtained by his procedure under which our values were obtained differs from those of Mr. Hamilton in temperature, furnace arrangement and material analyzed. It would be interesting to know whether he has analyzed material of higher manganese content, that is, in the range of 0.7 to 1.2 per cent, without finding any difference in the results obtained with an empty crucible and with a crucible containing a residue from a previous determination.

N. HAMILTON (written discussion).—Apparently no difficulty was experienced with manganese interference in the degasification of 18-8 alloys. The maximum

* U. S. Bureau of Standards.

¹⁹ H. C. Vacher and L. Jordan: U. S. Bur. Stds. *Jnl. of Research* (August, 1931) 375-401.

manganese content of any of the 18-8 alloys analyzed was 0.47 per cent. We have had some difficulty with manganese interference in carbon-iron-manganese alloys with manganese contents around 1 per cent, but careful initial heating and dilution of the high-manganese sample with a lower manganese degasified melt appears to take care of this condition. It is possible that the added alloy content of 18-8 decreases the volatilization of manganese in the sample.

C. H. HERTY, JR.,* Pittsburgh, Pa.—It might be worth while to investigate the oxygen in this steel by the method described by Reeve; that is, fractional distillation, where different percentages of oxygen are obtained by distillation at certain critical temperatures (p. 82, this volume).

There are no intermediate values given for oxygen. I suppose a series of very good heats and a series of very bad ones were chosen for this comparison. How did the intermediate oxygen heats behave? Did some of them slightly crack, or was there any sharp dividing line?

N. HAMILTON.—We did some work on the adaptation of Reeve's method of fractional distillation to this alloy but no definite conclusions were reached other than the fact that higher degasification temperature ranges were needed. It is true that a portion of the oxide is reduced at lower temperatures but our work at various degasification temperatures seemed to indicate that there was no sharp dividing line between complete reduction of the oxides present and selective reduction of some more easily reduced oxide. Another difficulty in connection with this work was the preparation of samples with known oxide combinations.

The question concerning intermediate values I believe is answered by Table 2, wherein it is noted that the minimum value for heats showing outside checking is 0.0106 per cent oxygen, while the maximum value for good material is 0.0087 per cent oxygen.

M. A. GROSSMANN,† Chicago, Ill.—It would be of interest to know what range of chromium and nickel and carbon contents was studied here, because of the possibility of the presence of high-temperature ferrite, which is known to lead to difficulties sometimes, although I believe not the type of difficulty shown by Mr. Hamilton; that is, not transverse outside checking.

N. HAMILTON.—All of the materials of this investigation contain a small amount of ferrite. This condition is confined to the core of the billet and has been assumed to be caused by a slight amount of nickel segregation, possibly the remnants of dendritic coring. We have been led to believe that this condition is responsible for some inside trouble in piercing but we have not associated it with the outside checking discussed in the paper. From our observations we would say that the outside and inside conditions are not related and the inside trouble is not associated with oxygen content.

As for analysis of the 18-8 materials, all were very uniform, with the ranges for chromium, nickel and carbon given in Table 4. The tendency for slightly higher chromium and lower nickel contents in the bad heats is explained by the fact that a number of the bad heats were made early in the investigation, when we did not fully realize the value of higher nickel-chromium ratios in reducing the amount of ferrite in the low-carbon alloy.

* Director of Research, Mining and Metallurgical Advisory Boards to the Carnegie Institute of Technology.

† Illinois Steel Co.

TABLE 4.—*Analysis of 18-8 Alloys*

	Good Heats			Bad Heats		
	Average	Max.	Min.	Average	Max.	Min.
Chromium, per cent.....	17.77	18.18	17.14	17.90	18.42	17.19
Nickel, per cent.....	9.10	9.98	8.48	9.01	9.52	8.42
Carbon, per cent.....	0.056	0.070	0.042	0.053	0.072	0.040

A. B. KINZEL,* New York, N. Y.—It would be interesting to have Mr. Hamilton tell more about the method of taking samples from billets or tubes.

N. HAMILTON.—In sampling tube billets, say of 5-in. diameter, it is necessary to include representative amounts of both core and rim material. It was found during the course of the work that a much more satisfactory sample could be obtained from a tube.

A. B. KINZEL.—That raises the question as to whether or not the high oxygen may be cause or effect.

N. HAMILTON.—I believe Dr. Herty mentioned that point a few days ago. The answer is that so far as we can tell there is no oxygen pick-up in piercing for in a number of cases we have found excellent agreement between the oxygen values of a heat both before and after piercing in the case of both high and low-oxygen materials. In all cases, at least $\frac{1}{16}$ in. is filed off the surfaces in the preparation of the samples.

G. B. WATERHOUSE,† Cambridge, Mass.—There is just one very natural question that comes to a man who has been operating, and that is whether advantage is being taken of this wonderful correlation of research work with the results of practice, whether it is being put into practical operation and is of practical value in the plant.

N. HAMILTON.—This work was originally designed to provide a method of plant control; however, it was found that a number of other steel defects were encountered in this material that were not indicated by oxygen content, so that it became more practical to run pilot rollings of the material from each heat. This oxygen correlation therefore became an explanation for one particular type of defect and not a complete answer to the problem of good piercing quality 18-8. The problem of manufacturing alloys of this type suitable for tube piercing we have relegated to our steel sources and I might say that they do a very good job. It must be remembered that the data in the paper are a result of some six years of experience in tube fabrication and starts with some of the first heats made into tubes.

S. L. HORT,‡ Milwaukee, Wis.—I should like to ask Mr. Hamilton to give us his ideas on the mechanism whereby these amounts of oxygen or chromium oxide produce the effect.

N. HAMILTON.—I am afraid I cannot contribute very much in way of explaining the mechanism of the effect of high oxygen upon the ductility of these materials in piercing. It so happens that every theory that has been offered has obvious faults and the fact that this phenomenon occurs at extremely high temperatures, about

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† Professor of Metallurgy, Massachusetts Institute of Technology.

‡ Research Metallurgist, A. O. Smith Corporation.

1200° C. (2192° F.) makes the experimental attack to the problem difficult. The examination of the inclusions present in these alloys at room temperature would indicate that some great change in state must occur at elevated temperatures in order to cause the observed results.

S. L. HORT.—Would you be willing to say that it relates to the condition of the steel rather than to its cleanliness?

N. HAMILTON.—The results of the work have indicated that certain combinations of oxygen in the material do not affect the elevated temperature ductility in the piercing range. These combinations are presupposed from the knowledge of the oxide-forming elements present and have not been definitely established by analysis.

S. L. HORT.—I think this discussion must suggest that people like Professor Waterhouse, who has had the exceptional opportunity of studying both the practical and academic work, might very well take up a problem like this as a fundamental study and might very well start with something as simple as pure iron, and go from there to some of the alloy steels. There is some very valuable, fundamental information relating to the manufacture and behavior of steels that is lacking, which our academic research establishments might very well take up as research problems.

F. N. SPELLER,* Pittsburgh, Pa.—We have a highly efficient organization in Pittsburgh under the Metallurgical Boards that are studying oxygen and its effects on steel, and I would suggest that Dr. Herty make a note of this interesting problem in connection with the proposed extension of this cooperative work that we are now considering. We have never felt it necessary to go to the length that they have in Germany in making heats in vacuum in order to eliminate all the gases. The trouble referred to occurs only occasionally. I think Mr. Hamilton will bear me out in that. I would like to ask Dr. Herty if he can predict how much dissolved oxygen there would be present under these conditions. The application of these principles to the manufacture of seamless steel tubing has materially improved the practice in recent years.

C. H. HERTY, JR.—Dr. Speller has asked me a difficult question. The answer is no, we have not enough data on it.

* Metallurgical Engineer, National Tube Co.

Titanium and Columbium in Plain High-chromium Steels

BY FREDERICK M. BECKET* AND RUSSELL FRANKS,† New York, N. Y.

(Detroit Meeting, October, 1933)

WIDESPREAD experimentation has been conducted in recent years to devise a means of preventing intergranular corrosion in austenitic chromium-nickel steels of the 18 per cent chromium-8 per cent nickel type. Additions of titanium to these steels have been used commercially to overcome this difficulty, as advocated by Krupp of Germany, and the latest literature reference concerning improved details of this method is the article by Bain, Aborn and Rutherford.¹ Extensive work by the present authors has shown columbium also to be a particularly valuable agent for inhibiting intergranular corrosion.

This paper does not deal with steels that are largely or wholly austenitic; it is limited to a discussion of the results obtained through the use of titanium and columbium in plain high-chromium steels. For many years titanium has been used commercially by some steelmakers as a cleanser, and to a lesser extent as a hardener, but then in greater percentages. The results of the work to be described disclose that titanium and columbium in proper proportions act as effective softeners in the high-chromium steels.

It is well known that chromium intensifies the hardening effect of carbon in steel; it imparts pronounced air-hardening properties within a rather wide range of chromium content; it provides increased ductility in steels of given strength and hardness; and it enhances resistance to corrosion and oxidation at elevated temperatures to a marked degree. However, in applications requiring a combination of some of these valuable properties great hardness is frequently a detriment rather than a merit. When the objective is a soft and ductile steel having optimum corrosion resistance, the producer strives for a carbon content as low as commercially practicable.

Despite these efforts some of the commercial high-chromium steels low in carbon present considerable difficulties during production, owing to their air-hardening properties, and in consequence the economic result is not favorable. A good example is found in the 5 to 6 per cent chromium steels employed chiefly in the oil-cracking industry. Steels

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¹ E. C. Bain, R. H. Aborn and J. J. B. Rutherford: Prevention of Intergranular Corrosion in Austenitic Stainless Steels. *Trans. Amer. Soc. Steel Treat.* (1933) 21.

containing appreciable percentages of chromium are sluggish in their thermal changes, and comparatively long periods are required for annealing. There are many applications in which the plain chromium steels would prove exceedingly useful if greater softness and more ductility could be obtained together with substantial freedom from air-hardening, all without sacrificing resistance to corrosion and oxidation at high temperatures.

With the definite purpose of overcoming the air-hardening tendency and imparting other desired characteristics, an extensive investigation has been made by the authors in which different elements known to have a strong affinity for carbon have been alloyed with steels containing relatively small to large percentages of chromium. Columbium, tantalum, titanium, zirconium, vanadium, tungsten, molybdenum, and other elements have been added in sufficient proportions to combine with the carbon present in the steels; also, each element has been introduced in excess of this requirement in order to determine its effect on the iron-chromium solid solution.

Of the metals employed as addition agents in this investigation columbium and titanium have proved the most efficacious. For the sake of brevity a few comments must suffice concerning the influence of the other metals.

Tungsten and molybdenum additions inhibited air-hardening slightly. The carbides of these metals are fairly soluble in iron-chromium solid solution, and on cooling from high temperatures these carbides precipitate in finely divided form, preventing the steel from becoming soft and ductile in the hot-rolled condition. Of course the high-chromium steels containing tungsten or molybdenum can be softened through proper annealing, a fact true also of untreated plain chromium steels.

Suitable proportions of zirconium, tantalum, and vanadium afford greater improvement than do tungsten and molybdenum, but certain practical disadvantages must be considered. Approximately twenty times as much tantalum as carbon is required in the steels for satisfactory results—a cost unwarranted commercially. Vanadium must be used in a ratio of about fifteen to one of carbon, but this relatively high percentage decreases the resistance of the steels to oxidation at high temperatures. It is true also that zirconium is required in relatively large percentages to sufficiently diminish air-hardening, but the large addition introduces undesirable proportions of silicon into the steels, if the relatively inexpensive zirconium alloys are employed.

The results obtained through additions of titanium and columbium were decidedly interesting—indeed, they were surprising. Titanium should be present in a ratio of five to seven times the percentage of carbon, and for columbium a ratio of eight to ten is required. Although it should be understood that smaller ratios afford some improvement, large excesses

of titanium and columbium over the recommended ratios bring about detrimental effects through hardening of the solid solution of iron and chromium.

One of the marked characteristics of the plain high-chromium steels containing titanium or columbium is the facility with which they may be hot-worked, a result of freedom from the air-hardening tendency.

The physical properties of some of the wrought steels containing titanium are presented in Table 1. It should first be observed that in the as-rolled condition the low-carbon steel containing about 3 per cent

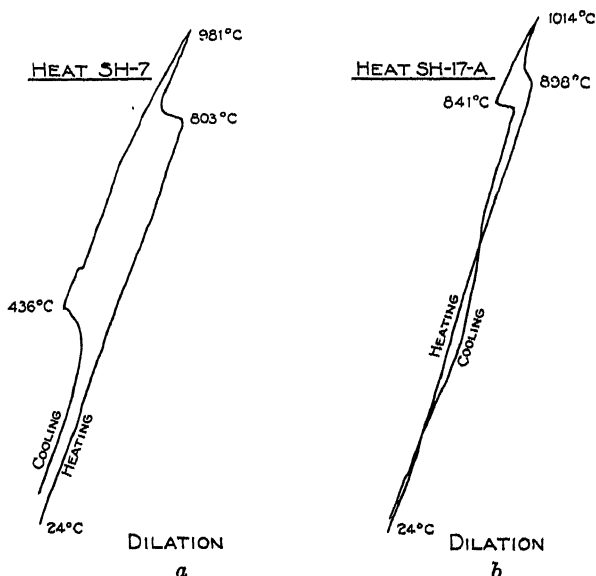


FIG. 1.—CRITICAL-POINT DETERMINATIONS, SHOWING INFLUENCE OF TITANIUM ON CHROMIUM STEELS.

a. This steel contains 5.56 per cent chromium and 0.10 per cent carbon. The A_{c1} point is at 803°C ., while on cooling the A_{r1} point is not reached until the temperature drops to 436°C ., showing that the steel air-hardens.

b. This steel contains 5.93 per cent chromium, 0.13 per cent carbon, and 0.90 per cent titanium. The addition of the titanium has raised the A_{c1} point to 898°C ., while the A_{r1} change is completed when the temperature falls below 841°C . This curve explains the effect of titanium in reducing air-hardening properties.

chromium is comparatively ductile and soft, whereas by reason of air-hardening the 5 per cent chromium steel is relatively hard and considerably less ductile. Here emphasis should be laid on the marked difference in physical properties between the untreated (substantially titanium-free) and the titanium-bearing steels, both in the as-rolled condition. As an example, the ductility and softness of the 5.41 per cent chromium steel containing 0.11 per cent carbon and 0.75 per cent titanium are not approached in the as-rolled condition by a steel of similar analysis without titanium. The commercial value of this difference need not be emphasized.

The properties of the titanium-bearing steels can be further improved through annealing at temperatures between 700° and 900° C.; and, to stress a point of practical importance, this may be accomplished by holding the steels for only a few minutes at temperatures approaching the upper limit of this range. Annealing at temperatures much above 900° C. greatly decreases the toughness, although the steels are not in this way appreciably hardened.

Similar results are shown in Table 1 for the low-carbon titanium-treated 12 to 14 per cent chromium steels. The effectiveness of titanium is particularly demonstrated in the two 13 per cent chromium steels

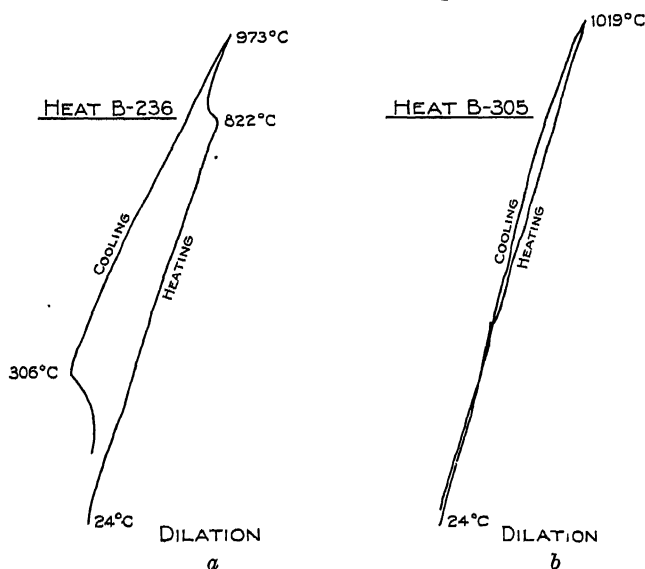


FIG. 2.—CRITICAL-POINT DETERMINATIONS, SHOWING INFLUENCE OF TITANIUM ON CHROMIUM STEELS.

a. This steel contains 13.17 per cent chromium and 0.12 per cent carbon. The A_{c1} point occurs at 8.22° C. but the change on cooling does not complete itself until a temperature of 306° C. is reached.

b. It is interesting to note that by the addition of 0.72 per cent titanium to a steel containing 0.14 per cent carbon and 12.37 per cent chromium, the critical changes on heating and cooling from temperatures as high as 1019° C. are eliminated for practical purposes.

containing respectively 0.34 and 0.58 per cent carbon. These examples are cited for their interest, but it should not be inferred that the full titanium treatment is advocated for chromium steels so high in carbon.

Table 3 gives the figures obtained from titanium-bearing steel plates of $\frac{1}{2}$ in. thickness containing 6 and 13 per cent chromium. These plates were rolled in a commercial mill from 4 by 4-in. billets, which were forged from 6 by 6-in. ingots.

The influence of titanium on the 5 to 6 per cent and the 12 to 14 per cent chromium steels is explained by the graphs in Figs. 1 and 2, representing critical-point determinations.

TABLE 1.—Physical Tests on Plain Chromium Steels Containing Titanium and Columbium

STANDARD TEST PIECES TAKEN FROM 1-IN. ROUND BARS

Cr, Per Cent	C, Per Cent	Ti, Per Cent	Cb, Per Cent	Condition of Metal	Yield Point, Lb. per Sq. In.	Max. Stress, Lb. per Sq. In.	Elonga- tion, Per Cent in 2 In.	Red. of Area, Per Cent	Izod Impact Ft.-lb.	Erich- sen Value	Brinell Hard- ness
3.05	0.07			As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	53,000 43,000	80,000 60,000	22 43	64 81	72 96	6.9 8.8 7.3	126 116
3.22	0.09	0.73		As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	46,000 37,000	72,500 68,000	31 28	74 75	86 111	8.2 9.5 10.0	126 116
5.44	0.10			As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	149,500 74,000	181,000 92,500	5 26	12 74	22 94	5.5 7.9 5.5	375 153 340
5.41	0.11	0.75		As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	84,000 28,000 29,000	100,000 61,000 62,000	18 37 44	68 78 79	24 63 112	6.3 9.0 9.5	163 112
5.62	0.09		1.04	As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	98,000 32,000 61,000	111,000 62,000 82,000	16 29 27	62 78 70	59 108 105	6.0 8.1 8.0	192 143
13.60	0.13			As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	149,000 61,000 117,000	204,000 91,000 149,000	3 24 4	8 60 6	30 68 8	5.0 8.4 3.5	418 143 241
13.35	0.11	0.85		As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	38,000 39,000 36,000	63,400 63,400 64,000	25 28 33	70 75 70	10 22 30	6.7 8.8 9.4	126 112 112
12.42	0.10		1.18	As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 10 min. and air-cooled.....	39,200 37,000 39,000	63,300 37,000 63,000	20 31 37	53 65 73	15 37 77	6.8 7.6 9.2	121 116 112
13.32	0.34	1.76		As rolled..... Heated at 1000° C. 5 min. and air-cooled.....	49,000 44,000	76,000 74,500	25 27	55 53	3 15	6.3 8.6	143 124
13.34	.56	2.13		As rolled..... Heated at 1000° C. 5 min. and air-cooled.....	64,000 55,600	100,000 83,000	21 26	47 51	3 4	6.0 7.7	179 159

TABLE 2.—*Physical Tests on 18 and 26 Per Cent Plain Chromium Steels Containing Titanium and Columbium*
STANDARD TEST PIECES TAKEN FROM 1-IN. ROUND BARS

Cr, Per Cent	C, Per Cent	Ti, Per Cent	Cb, Per Cent	Condition of Metal	Yield Point, Lb. per Sq. In.	Max. Stress, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Red. of Area, Per Cent	Brinell Hardness	Erich- sen Value
18.29	0.07			As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 20 min. and air-cooled..	57,000 51,000 59,000	92,500 83,500 97,000	7 30 9	14 55 18	170 143 159	5.5 7.5 6.0
18.65	0.13	0.78		As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 20 min. and air-cooled..	49,000 50,000 40,000	71,500 76,000 68,000	31 29 32	69 66 66	131 131 118	7.0 7.0 9.0
19.20	0.07		1.00	As rolled..... Heated at 750° C. 4 hr. and air-cooled..... Heated at 900° C. 20 min. and air-cooled..	52,000 43,000 45,000	72,000 69,500 72,000	22 31 29	41 65 63	149 137 118	6.5 8.0 8.5
26.28	0.14			As rolled..... Heated at 875° C. 12 hr. and water- quenched..... Heated at 900° C. ½ hr. and air-cooled..	62,000 56,000 49,000	89,000 83,000 66,000	9 26 5	11 51 6	187 159 137	6.0 8.0 7.9
26.90	0.18	1.20		As rolled..... Heated at 875° C. 12 hr. and water- quenched..... Heated at 900° C. ½ hr. and air-cooled..	66,000 57,000 58,000	86,500 83,000 83,000	29 26 28	64 56 58	163 137 143	7.0 8.0 8.5

TABLE 3.—Physical Tests on $\frac{1}{2}$ -in. Plates of 6 and 13 Per Cent Plain Chromium Steels
ROLLED IN COMMERCIAL MILL

Cr, Per Cent	C, Per Cent	Ti, Per Cent	Mn, Per Cent	Si, Per Cent	Condition of Metal	Yield Point, Lb. per Sq. In.	Max. Stress, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Red. of Area, Per Cent	Izod Impact, Ft.-lb.	Brinell Hard- ness	Rockwell B Hardness
5.93	0.13	0.90	0.56	0.39	As rolled..... Heated at 900° C. 10 min. and air-cooled.....	39,800	66,100	34	68	69	128	86
13.35	0.11	0.85	0.46	0.19	As rolled..... Heated at 900° C. 10 min. and air-cooled.....	34,200 44,300 36,000	67,100 66,000 59,400	37 35 34	68 60 70	74 28 51	112 126 112	63 88 63

In Fig. 1 the left-hand graph reveals that the critical change on heating occurs at 803° C. in the untreated 5.56 per cent chromium steel. On cooling the same steel the A_{r1} point is reached only when the temperature drops to 436° C. The right-hand graph depicts the result of heating the titanium-treated 5.93 per cent chromium steel to 1000° C. and cooling it therefrom. It should be noted that the A_{c1} point is raised from 803° to 898° C., whereas on cooling the A_{r1} change is completed at 841° C. The difference between the graphs explains the non-hardening ability of the titanium-treated steels. Furthermore, the graphs reveal that heating for a few minutes at 900° C. followed by air-cooling provides the annealing treatment most advantageous for the steel containing titanium.

The results of critical-point determinations on titanium-treated and untreated 13 per cent chromium steels are plotted in Fig. 2. Again it should be observed that the changes occur in the untreated steel over a wide range of temperature, whereas the presence of titanium practically eliminates the change points that normally occur on heating and cooling the 13 per cent chromium steels from temperatures up to about 1000° C.

Metallographic examination provides useful confirmatory information. The photomicrographs of Figs. 3 and 4 show that the hot-rolled, untreated 5.44 and 13.60 per cent chromium steels possess structures of the martensitic type. Annealing for 4 hr. at 750° C. modifies these structures, the carbides coalescing to larger particles. Heating the same steels to 900° C. and air-cooling renders them substantially martensitic, relatively hard and brittle. The decided difference

in structure induced by the introduction of titanium is clearly shown in the associated photomicrographs. Chromium ferrite and carbides are the principal constituents and represent a type of structure not appreciably

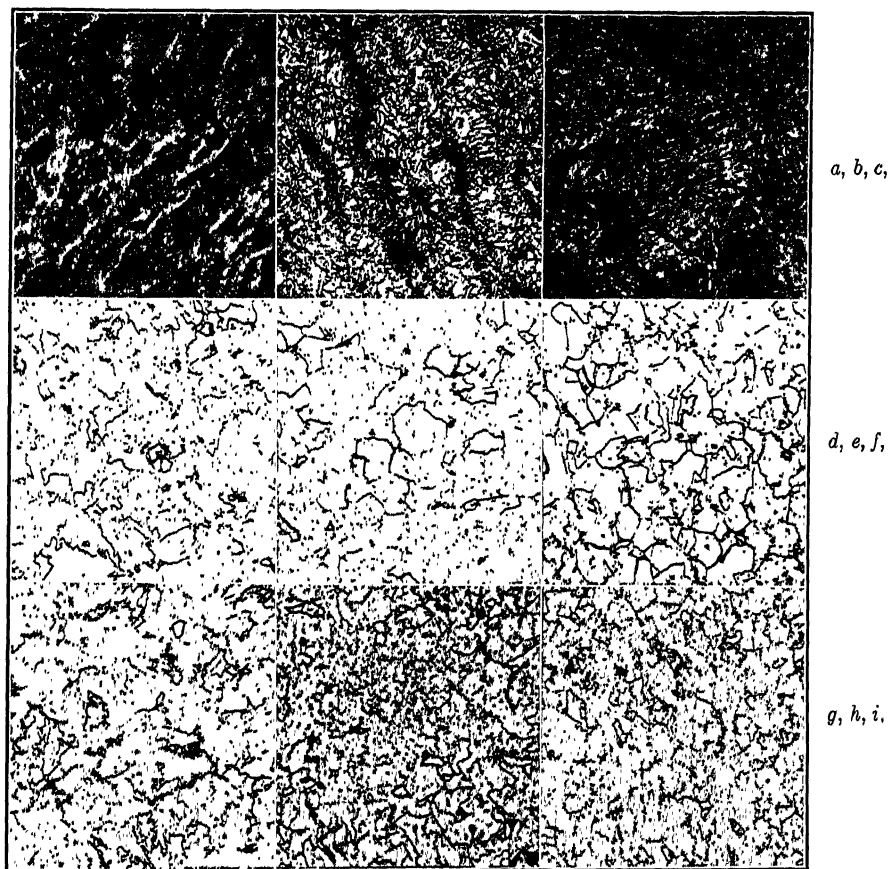


FIG. 3.—EFFECT OF TITANIUM AND COLUMBIUM ON STRUCTURES OF 5 PER CENT CHROMIUM STEELS.

- a. 5.44 per cent chromium, 0.10 per cent carbon steel as hot-rolled.
- b. Same steel after 4 hr. at 750° C. and air-cooling.
- c. Same steel air-hardened from 900° C.
- d. 5.44 per cent chromium, 0.11 per cent carbon, 0.78 per cent titanium steel as hot-rolled.
- e. Same steel after 4 hr. at 750° C. and air-cooling.
- f. Same steel after 10 min. at 900° C. and air-cooling.
- g. 5.62 per cent chromium, 0.10 per cent carbon, 1.04 per cent columbium steel as hot-rolled.
- h. Same steel after 4 hr. at 750° C. and air-cooling.
- i. Same steel after 10 min. at 900° C. and air-cooling.

All $\times 300$.

changed by heating to temperatures even as high as 1000° C. Does it not seem reasonable to conclude from the foregoing that the carbides formed by the addition of titanium or columbium are not sufficiently soluble in the

iron-chromium solid solution to form austenite? Indeed, it has been determined through experimental work that these carbides are almost completely insoluble in the solid solution.

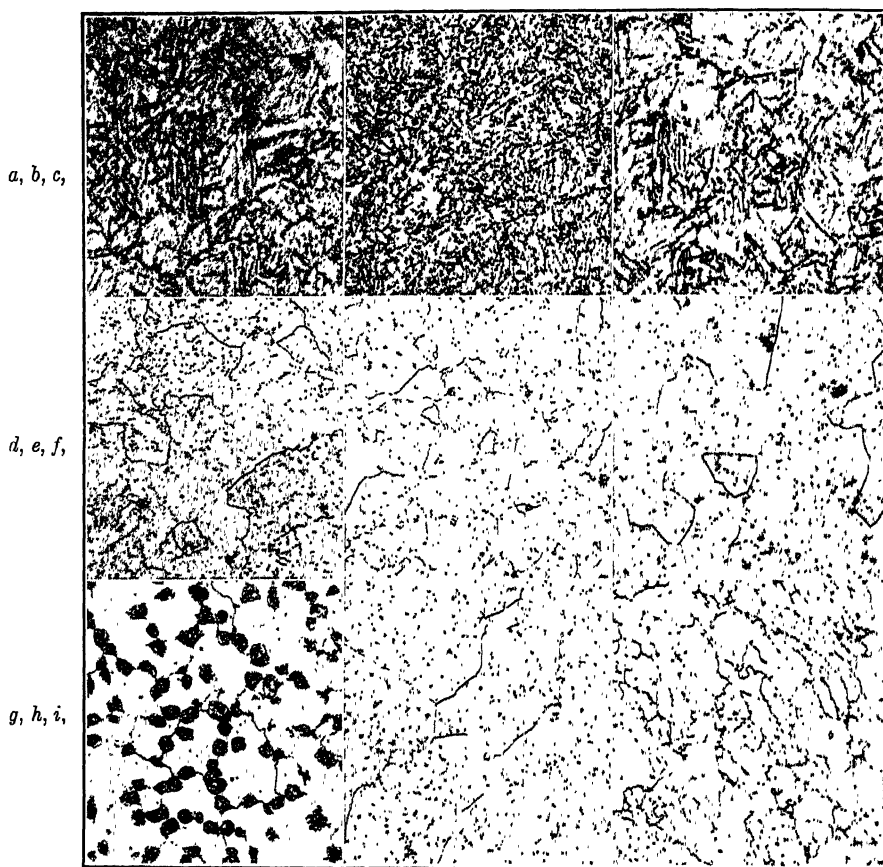


FIG. 4.—EFFECT OF TITANIUM AND COLUMBIUM ON STRUCTURES OF 13 AND 18 PER CENT CHROMIUM STEELS.

- a. 13.60 per cent chromium, 0.13 per cent carbon steel as hot-rolled. $\times 300$.
- b. Same steel after 4 hr. at 750°C . and air-cooling. $\times 300$.
- c. Same steel air-hardened at 900°C . $\times 300$.
- d. 12.32 per cent chromium, 0.14 per cent carbon, 0.72 per cent titanium steel as hot-rolled. $\times 100$.
- e. Same steel after 4 hr. at 750°C . and air-cooling. $\times 100$.
- f. Same steel after 10 min. at 900°C . and air-cooling. $\times 100$.
- g. 18.29 per cent chromium, 0.06 per cent carbon steel after 4 hr. at 750°C . and air-cooling. $\times 100$.
- h. 18.65 per cent chromium, 0.13 per cent carbon, 0.78 per cent titanium steel after 10 min. at 900°C . and air-cooling. $\times 100$.
- i. 18.23 per cent chromium, 0.12 per cent carbon, 1.18 per cent columbium steel after 10 min. at 900°C . and air-cooling. $\times 100$.

Table 2 gives the results obtained from treated and untreated low-carbon 18 and 26 per cent chromium steels. It is well known that although these plain chromium steels are not of the hard variety after

hot-rolling, low ductility is characteristic; furthermore, it is known that comparatively long annealing periods are required to improve their ductility. A significant effect of the titanium addition is again brought out; because, in addition to the softness of these steels in the hot-rolled condition, the annealing period required to further improve the properties is of short duration, and the steels finish with greater ductility and softness than those lacking titanium. Photomicrographs of annealed 18 per cent chromium steels with and without titanium and columbium are shown in Fig. 4. A discussion seems unnecessary in view of the structures described for the lower chromium steels containing titanium.

All these steels have been subjected to the generally accepted corrosion tests. The results disclose that in steels containing less than about 12 per cent chromium an appropriate addition of titanium augments the resistance to oxidizing media. Less pronounced in this respect is the effect of titanium in the higher chromium low-carbon steels, no doubt because they are inherently more resistant under oxidizing conditions.

Tests have been conducted under atmospheric conditions embracing titanium-treated and untreated low-carbon 5, 6, 7.5 and 9 per cent chromium steels. These samples and others of the higher chromium groups have been exposed for a long period of time. Briefly, the most important feature uncovered by these tests is that through the agency of titanium there appear interesting commercial possibilities for a steel containing 7 to 9 per cent chromium—a steel not completely resistant to staining but nonetheless one which affords a great measure of protection against progressive rusting. Even without annealing, the combined properties of steel of this class are such as to indicate numerous commercial applications.

The various groups of plain, high-chromium steels discussed in this paper are all employed commercially at elevated temperatures. For this use the advantages accruing from the addition of titanium are most prominently developed in the steels of the lower chromium varieties. Taking the single case of exposure to 750° C., it is observed from Fig. 5 that titanium considerably increases the resistance to oxidation of the 5 to 6 per cent chromium steel. Weekly removal of the scale is unfavorable to titanium in the relationships shown, but this method presented opportunities to observe that titanium-treated steels of this class have a more adherent scale. Moreover, these titanium-treated steels retain their toughness after relatively long periods at temperatures up to 650° C., the highest temperature at which the toughness tests have so far been conducted.

The accuracy of creep-testing methods is still under rigorous investigation and discussion, and probably the 4 to 6 per cent plain chromium steels containing additions of molybdenum and tungsten played a leading part in raising the controversy. Therefore the following data are pre-

sented with reservations, realizing that additional work should be performed. In creep tests at 538° C. a titanium-treated 5.93 per cent chromium steel withstood a load of 10,250 lb. per sq. in. without creeping more than 1 per cent in 10,000 hr. The addition of 0.50 per cent molyb-

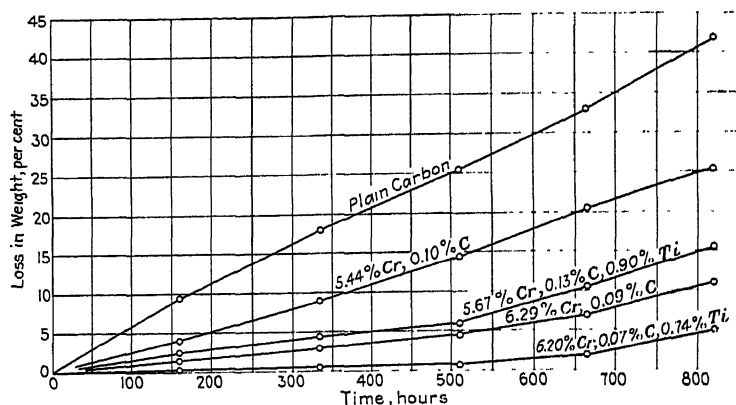


FIG. 5.—RESULTS OF OXIDATION TESTS ON TITANIUM-TREATED AND UNTREATED CHROMIUM STEELS AT 750° C.

denum or 1 per cent tungsten had little influence on the creep strength of the metal at this temperature.

Plain low-carbon 18 per cent chromium steels continue to render excellent service in many applications. An improvement greatly desired is

TABLE 4.—Tests on 18 Per Cent Plain Chromium Steel Strip Containing Titanium

Cr, Per Cent	C, Per Cent	Ti, Per Cent	Condition of Metal	Rockwell B Value	Brinell Value
18.65	0.11	0.65	As hot-rolled 0.080-in. strip.....	90	
			Heated at 900° C. 10 min. and air-cooled..	73	
			Cold-rolled from 0.08 to 0.04-in. thick strip	99	6.8
			0.04-in. strip heated 10 min. at 750° C. and		
			air-cooled.....	77	10.5
			0.04-in. strip heated 10 min. at 850° C. and		
			air-cooled.....	74	10.5
			0.04-in. strip heated 5 min. at 900° C. and		
			air-cooled.....	73	11.0
			0.04-in. strip heated 2 min. at 1000° C. and		
			air-cooled.....	74	10.9

increased softness and amenability to deep-drawing operations, particularly by the fabricator, and the addition of titanium to this steel assists considerably in this direction. Some of the properties of titanium-bearing steels of this class are shown in Table 4.

Admittedly all these titanium-containing plain chromium steels present difficulties in welding similar in some respects to those often found in the welding of 18 per cent chromium-8 per cent nickel steels containing titanium. Realization of this problem afforded the stimulus for intensive experimental work in welding the new steels here described. That the experiments are yielding very encouraging results is all that should now be stated.

Titanium has dominated the foregoing description. However, it should be emphasized that all the beneficial effects obtained by this element have been secured also through the addition of columbium, a metal which in the form of a ferroalloy can be incorporated with high recovery under good melting practice appropriate to the high-chromium steels.

Considering the results of the experimental and commercial work performed it seems reasonable to conclude that titanium or columbium will permit the introduction of a new chromium steel and so facilitate the production of the plain high-chromium steels as to broaden their field of utilization.

ACKNOWLEDGMENT

The authors desire to express their appreciation of the enthusiastic cooperation received from several members of the staff of Union Carbide and Carbon Research Laboratories: Mr. James Thompson and Mr. W. L. Harbrecht for the making of steel ingots; Mr. T. R. Cunningham and Mr. R. J. Price for special analytical chemistry; Mr. J. R. Vilella for his work in metallography; and Mr. Fred Bacon for his corrosion tests.

DISCUSSION

(John Johnston presiding)

V. N. KRIVOBOK,* Pittsburgh, Pa.—Mr. Franks, in presenting the paper, stated that there are two sides pertaining to this work, one of the possible commercial uses and applications, and the other of a purely theoretical nature. I shall not attempt to discuss the first phase, but there are several questions of theoretical nature which are of much interest to me. My discussion should be interpreted as mere suggestions, and, therefore, absolutely devoid of the spirit of criticism.

I have done a fairly large amount of work on this class of steels, especially in the field of phase changes, using the dilatometric method, supplemented by microscopic studies. Knowing the importance of certain details of procedure, I was somewhat disturbed when I failed to find in the paper the rates of either heating or cooling operations used to determine the temperatures of phase changes. And furthermore, Dr. Becket and Mr. Franks state (p. 128) that the reaction on cooling went to completion. I beg to be allowed to disagree with the last statement. I have repeatedly found that in alloys of this general type the reaction goes to completion only under rather unusual experimental conditions. The position of phase change on simple

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cooling is altogether a question of rate, together with other experimental circumstances. From the paper I find that critical points for 6 per cent chromium (Fig. 1) and for 12 per cent chromium (Fig. 2) can be placed approximately at 400° to 436° C. for the former and 300° C. for the latter. The same reaction can be (and was) made to take place at a much higher temperature if the rates of cooling are only 6° C. per minute—not an extremely slow rate. Consequently, the figures that Mr. Franks gives indicate a rapid rate of cooling, with the almost certain conclusion that the reaction is far from being completed.

I was also very much interested in the appearance of the dilation curve for the alloy of 6 per cent chromium given in Fig. 1b. That curve shows that the heating and cooling curves intersect each other. Three possibilities may be entertained: (1) that something went wrong with the apparatus, and I trust that the authors will forgive me this suggestion since I know only too well how easily such things can happen when one works with the dilatometer; (2) that the curve was taken from the sample in hot-rolled condition; and (3), intimately connected with number 2, that some reaction is taking place on cooling, and needs to be studied. If I may suggest, careful experiments on holding alloys within certain ranges of temperature will indicate whether or not the observed abnormality is experimental error or the real state of affairs.

The curve for 13 per cent chromium alloy containing titanium is very typical of that of low-carbon, low-nitrogen 18 per cent chromium. We know by this time that nitrogen has a definite effect, not only on the phase changes, that is, on the temperature of the critical points, but also on the properties of this type of steels. And this consideration brings immediately to my mind the question of advisability of including in the chemical analysis the figures for nitrogen content. Also, the analysis for nickel should be very desirable, because in steels containing either 13 or 18 per cent chromium, even slight difference in nickel content, let us say 0.25 as against 0.50 per cent, has a definite influence—and I feel quite safe in stating it—not only on the temperatures and magnitude of the phase changes but of course on the properties of the metal as well. I happen to know that the interest in this paper runs very high and that there are in the audience several gentlemen desirous of discussing it. So I shall curtail my remarks. May I state once more that these remarks are offered in the friendly nature of suggestion and not at all as criticism. I fully appreciate how difficult it is to present a new subject of such broad interest in, necessarily, a comparatively short paper of this sort.

W. B. ARNESS,* Baltimore, Md.—The present wide discussion of the effect of titanium and columbium on the 18-8 alloy has made the presentation of this paper most timely. The authors are to be sincerely congratulated for having developed these most interesting new data.

The authors treat their subject briefly, and do not deal at length with the fundamental metallurgy of their titanium-bearing alloys. However, the impression is gained that the authors have added a constituent to the iron-chromium alloys which has fixed the carbides in a stable form throughout the usually employed heat-treating temperature ranges. Thus we have in effect an iron-chromium alloy which behaves as we might suppose the ordinary alloy should behave if it were carbon-free.

The paper strikes me as being incomplete, and I am thus encouraged to ask the authors if they cannot supplement it somewhat. The work no doubt is well supported by experimental evidence, so that we can accept the summarized findings as presented. However, it is surprising to me that titanium carbide in the iron-chromium alloys should be spontaneously formed in such a stable form without any deliberate heat

* Melting Superintendent, Rustless Iron Corporation of America.

treatment, as is suggested by Fig. 4*l*. That photograph is of the 13 per cent chromium alloy in the hot-rolled condition. It shows a large-grained equiaxed structure which is not what we usually obtain in hot-rolling small bars. More often some distortion of the grain due to rolling strains is evident. In fact, all of the figures *d*, *e* and *f* of this 13 per cent chromium alloy are exactly what one might expect from a 17.0 or 18.0 per cent chromium alloy having extremely low carbon, and, as Dr. Krivobok mentioned, low nitrogen content. They really bear a striking resemblance to figures *h* and *i* just below them, which do represent the 18.0 per cent chromium alloy. There is so very little difference between those five photographs that one is much impressed with this visible evidence of the effect of titanium, especially on the 13 per cent chromium alloy.

It would also be interesting, as Dr. Krivobok suggested, if we could have a more complete analysis. I would presume from the nature of the data that the nickel is quite low. We can probably also assume that the silicon is within commercial limits, probably quite low. However, that might depend somewhat on the nature of the titanium alloy used. An analysis for aluminum would be interesting. That also might depend on the type of alloy used for adding titanium. Nitrogen we assume should probably be fixed by the titanium in the form of titanium nitride, thus taking it out of the alloy for all practical purposes, at least in so far as it would affect structural changes.

From reading the paper one might gain the impression that the effect of titanium is to render the iron-chromium alloys, at least the 13 and 18 per cent chromium alloys, rather coarse grained, low in hardening ability, lacking in the usual structural transformations. Also, evidence is presented that these alloys possess improved ductility and heat resistance. This is indeed interesting, because it is common experience that other additions, as for instance small amounts of nitrogen, have exactly opposite effect and yet produce much the same result. The effect of nitrogen is to refine the grain, increase hardenability, retard grain growth and decarbonization. Its net result on the alloy is to improve ductility as for deep drawing, and improve heat resistance. A further elaboration of the data presented in the paper would, no doubt, do much to clarify and harmonize these points.

As for the low hardness and low tensile strength values recorded in the paper, these properties can be approached by merely lowering the carbon of the 13 per cent chromium alloy to about 0.05 or 0.06 per cent, and holding the nitrogen very low. In this way, we can pull the hardenability down from a normal figure of 375 to 400 Brinell to about 275 to 300 Brinell maximum, and so without any addition—on the contrary, merely by subtracting carbon—we can actually produce a similar effect on these alloys.

Some of the reported hardness values bother me a little because the Brinell and Rockwell comparisons do not appear at first glance altogether consistent. In Table 3, for instance, 126 Brinell corresponds to 88 Rockwell B. I have been accustomed to compare Rockwell 88-B with 170 Brinell or higher. Of course, conversion of Rockwell to Brinell is not particularly consistent or satisfactory on these alloys, anyway, and the peculiar structures shown may explain this discrepancy.

Again, in Table 4, the figures for strip are normal for ordinary strip of 18 per cent chromium alloy. We often obtain hot-rolled strip that shows 90 Rockwell B. Similarly, after cold rolling, Rockwell 99-B represents about the maximum hardness obtained. Sometimes the hardness may go up to 103 Rockwell B, but this is not substantially harder than shown in the table.

The figures for annealed strip are normal also (Table 4). We can go down to 73 and 77 Rockwell B without difficulty, although the heat treatment used by the authors is somewhat unorthodox, suited no doubt to the unique nature of these new alloys.

Erichsen values reported by the authors are rather high in some cases, but it would be helpful if the gage of the material were mentioned as well.

From the data presented, the impression might be gained that the 13 per cent chromium alloy with titanium resembles closely in structural behavior and even in physical properties the normal 17 or 18 per cent chromium alloy, thus taking it entirely out of the class of the very useful 12 or 13 per cent chromium alloys. In fact, the range of analysis between say 0.05 to 0.15 per cent carbon, and 11.5 to 14.5 per cent chromium, comprises not one alloy, but a whole series of alloys, and there is much that we can still do in altering the usual recognized physical properties of this series of alloys by changing their analyses within these limits. Thus many special-purpose alloys may still be produced approaching on the one extreme low strength and low hardness, and on the other high strength and high hardness, without doing more than to juggle the proportions of the constituents present in the standard alloys.

I do not agree with the authors that the usual annealing treatments for the iron-chromium alloys are difficult or involved, and they certainly are not unusually expensive. This point may have some significance when it is realized that the properties of the 13 and 18 per cent chromium alloys discussed by the authors may be approached without having recourse to special additions, and the nominally higher strength and hardness possessed by the fully annealed standard alloys must be balanced against the difficulty and expense of making special additions.

The results reported in the paper are most interesting, and much more startling than we might expect through making the more ordinary modifications to the standard analyses. The paper clearly demonstrates that there is a pronounced effect from the use of titanium and columbium, and I clearly recognize that the value of these additions may be justified many times through experience as we come to know them better. At the present time, though, my personal inclination is to be a little bit conservative, and to withhold any opinion until a fuller knowledge of these alloys is available.

L. SCHAPIRO,* Chicago, Ill.—Essentially these are iron-chromium solid solutions without the attendant structures due to carbides. The changes in the A_1 points shown by the dilation curves can be explained on the basis of pure iron-chromium solid solutions. So that we might think of the addition of titanium and columbium as producing a material free from pearlite, whereas without such additions the steel would be pearlitic. Although the authors do not indicate that they are the innovators of this material, since this is, to my knowledge, the first technical paper on this subject we might look to them as such; and I want to make this particular point. I distinctly recall having in my files a copy of a patent issued 5 or 6 years ago to Professor Mathiesius in Germany covering the use of a titanium addition to simple steels to make them pearlite free.

F. M. BECKET and R. FRANKS (written discussion).—Dr. Krivobok's comments are greatly appreciated. Detailed information concerning the procedure employed in conducting the critical point determinations was not included in the paper for the sake of brevity. The determinations were made in a Rockwell dilatometer (model LA) on annealed samples of the different steels machined from 1-in. round bars to a length of 2 in. The hot end of the thermocouple was inserted in the center of the specimens. The individual samples were heated and cooled at the rate of 9° C. per minute, and the curves were obtained through the use of automatic equipment; also, the temperatures were recorded automatically. That each sample was investigated under approximately the same conditions is the important fact. We have no explanation for the fact that on heating and cooling the curves of Fig. 1b intersected each other in the vicinity of 500° C.

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Dr. Krivobok's criticism with reference to the statement that the reactions on cooling went to completion needs explanation. We realize that it is difficult to determine when such reactions fully complete themselves in steels of this type. The point in making this statement was merely to emphasize that the changes occurring in the titanium-containing steels took place at higher temperatures on heating and cooling than those taking place in similarly treated chromium steels without titanium.

His statements in regard to the effect of slight differences in nickel and nitrogen contents are answered by the analyses of Table 5.

TABLE 5.—*Analyses of Various Heats*

	Heat SH-7	Heat SH-17A	Heat 236	Heat B-305
Chromium.	5.56	5.93	13.17	12.37
Manganese	0.52	0.56	0.56	0.58
Silicon	0.32	0.39	0.38	0.41
Nickel	0.06	0.07	0.27	0.09
Carbon.	0.10	0.13	0.12	0.14
Titanium		0.90		0.72
Aluminum.	Less than 0.01	0.09	Less than 0.01	0.06
Nitrogen	0.012	0.006	0.031	0.027

These show that the compositions of the steels are sufficiently comparable to secure the effect of titanium. The small amount of aluminum in the steels from heats SH-17A and B-305 was incorporated in the metal through the ferrotitanium addition.

The comments by Mr. Arness relating to the incompleteness of the paper seem a little too severe. More than 100 steels containing different percentages of chromium, carbon, titanium, columbium, and other alloying elements were made and tested during this investigation. However, some of the technical societies having requested authors to present their data as briefly as possible, we frankly admit an attempt at brevity in writing the present paper.

Mr. Arness' statements regarding the low hardness and low tensile strength values recorded in the paper are quite true. We realize that in hot-rolled 13 per cent chromium steels containing 0.05 or 0.06 per cent carbon, Brinell hardness values of 275 to 300 are obtainable, but the steel will exhibit relatively low ductility. If the same steel is treated with sufficient titanium or columbium to combine with the carbon present, the metal will give a Brinell number in the vicinity of 128, accompanied by considerable ductility. These properties are further enhanced by annealing the steel containing titanium for only a few minutes at 900° C., which is not true in the case of the plain 12 to 14 per cent chromium steel. This is one of the major points of the paper, and Mr. Arness' inference that altering the compositions of steels containing 11.50 to 14.50 per cent chromium and between 0.05 and 0.15 per cent carbon will yield steels with similar properties to those secured by adding titanium or columbium is erroneous.

Mr. Arness seems to think that the Brinell and Rockwell B hardness values given for the different steels are inconsistent. These were the values actually obtained on the steels and there is no evidence pointing to the fact that they are incorrect. The Erichsen values reported were secured on sheet ranging in thickness between 0.036 and 0.039 in. The aluminum, nitrogen, and nickel contents of these steels have been answered in the reply to Dr. Krivobok's discussion.

It seems certain that Mr. Arness misconstrued the statements in the paper concerning the annealing of the iron-chromium alloys. We specifically stated that the chromium steels containing titanium could be annealed in a relatively short period at

somewhat higher temperatures than those ordinarily employed for the plain high-chromium steels. Take, for example, the 5 to 6 per cent chromium steels that are used at present in commerce. After hot rolling, a period of several hours is required at the proper annealing temperature, followed by slow cooling, to obtain the desired ductility and toughness. However, if the same steel is treated with sufficient titanium or columbium to combine with the carbon present it may be made softer and more ductile than the untreated steel, by annealing for only 5 or 10 min. at temperatures in the vicinity of 850° to 900° C., followed by either rapid or slow cooling. A similar annealing treatment is suitable for other high-chromium steels containing the proper proportions of titanium, and our belief is that such a treatment is more economical than one requiring long holding periods at somewhat lower temperatures.

Mr. Schapiro states that 5 or 6 years ago a patent was issued to Professor Mathesius in Germany, covering the addition of titanium to simple carbon steels to make them pearlite free. We are familiar with a patent issued to Professor Mathesius in which it is stated that through the use of titanium steel with superior elasticity can be secured, and to obtain this result titanium is added to practically carbon-free iron. Thus Professor Mathesius' object was to obtain the hardening effect of titanium on ferrite, while the present goal is to inhibit the hardening effect of carbon on a chromium-bearing ferrite by combining the carbon present with titanium.

Effects of Columbium in Chromium-nickel Steels

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(New York Meeting, February, 1934)

IN a recent article,¹ which described the softening effect of columbium in plain high-chromium steels, the authors stated that their investigations had shown columbium to be also a particularly valuable inhibitor of intergranular corrosion in steels of the 18 per cent chromium, 8 per cent nickel type. It is the purpose of the present paper to record some of the results obtained through the introduction of columbium to the austenitic chromium-nickel steels. The damaging effects of this type of corrosion have become so widely known as to restrict considerably the applications of the steels under consideration, and therefore there is little question of the importance of the goal to be attained.

Numerous contributions concerning the susceptibility of the austenitic chromium-nickel steels to intergranular corrosion have appeared during the past few years, and among others who have dealt constructively with the subject are such well-known authors as Strauss and Houdremont of Germany, Hatfield of England, and Bain in the United States. Different theories have been propounded as to the cause of intergranular corrosion, and various remedial measures have been proposed, the majority of which involve the use of addition agents. Titanium is the addition agent at present most generally employed, as suggested by Houdremont and modified as described by Bain, Aborn and Rutherford.²

Little has been published on the effects of holding these steels for long periods at the relatively lower temperatures in the presence of corroding media, and the effects have not been fully realized by producer and consumer.

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¹ F. M. Becket and R. Franks: Titanium and Columbium in Plain High-chromium Steels. *A.I.M.E. Tech. Pub.* 506 (1933).

² E. C. Bain, R. H. Aborn and J. J. B. Rutherford: Nature and Prevention of Intergranular Corrosion in Austenitic Stainless Steels. *Trans. Amer. Soc. Steel Treat.* (1933) **21**, 481-509.

In the investigation under consideration a large number of plain chromium-nickel steels having various proportions of chromium, nickel and carbon have been tested. Furthermore, many steels of this class have been tested in which columbium, tantalum and numerous other elements have been incorporated. All these steels have been held for long periods in the range between 300° and 900° C. and followed by testing in a boiling solution containing 6 per cent copper sulfate and 10 per cent sulfuric acid. Some of the corrosion tests also involved boiling in a solution of 65 per cent nitric acid. The effect of similar heat treatments on the physical properties of most of these steels was also studied.

TABLE 1.—*Tests on Plain Chromium-nickel Steels of Varying Compositions*
(All samples quenched from 1150° C. before testing)

Cr, ^a Per Cent	Ni, Per Cent	C, Per Cent	Approximate Temperatures within Range 300°-850° C. that Cause Subsequent Disintegration in Boiling Acidified Copper Sulfate, Deg. C.	Approximate Temperatures within Range 300°-850° C. that Cause Decrease in Izod Impact Values, Deg. C.
12.74	6.27	0.03	400 to 550	Not tested
12.82	12.80	0.04	400 to 550	Not tested
12.52	25.44	0.05	400 to 550	Not tested
18.23	8.49	0.04	400 to 550	Not tested
17.47	9.27	0.07	400 to 650	650 ^b to 850
18.45	8.56	0.12	400 to 750	550 ^b to 850
18.40	9.37	0.19	400 to 750	550 to 850
18.37	14.12	0.09	400 to 550	650 ^b to 850
20.42	11.87	0.09	400 to 550	650 ^b to 850
22.25	15.06	0.04	475 to 550	Not tested
22.32	20.38	0.05	475 to 550	750 to 850
27.32	25.19	0.07	475 to 550	Not tested

^a These steels also contained normal amounts of manganese, silicon, phosphorus and sulfur.

^b Holding for the same period at temperatures near the lower limit of this range causes only a slight decrease in toughness.

The reason for describing in this paper only the effects of columbium resides in the finding of the authors that all things considered this element offers the most satisfactory solution of the intergranular-corrosion problem.

All the steels used in these tests were cast into 2-in. square or 8-in. square ingots and then rolled into 1-in. round bars and different gages of sheet. The intergranular-corrosion tests were made on samples of 20-gage sheet quenched from 1150° C. This treatment was followed by holding the samples at temperatures of 300°, 400°, 475°, 550°, 650°, 750° and 850° to 900° C. for one hour, twelve hours, three days, five days, two

weeks, one month, two months, and in some instances for five months. All samples were then boiled in the above-mentioned acidified copper sulfate solution for at least 200 hr., unless failure occurred earlier. The tensile and impact test pieces were machined to standard dimensions from 1-in. round bars and were either quenched or air-cooled from 1150° C. previous to testing.

In view of the literature on the subject it seems advisable to describe some of the results obtained on the plain chromium-nickel steels. It should be noted in Table 1 that steels containing between 12 and 27 per cent chromium, 6 and 25 per cent nickel, and relatively low carbon content could be disintegrated after holding at temperatures between about 400° and 750° C., although the steels having the higher chromium and nickel contents with relatively lower carbon are subject to disintegration within a narrower range of temperature. However, it was found that the susceptibility of these steels to intergranular corrosion was not accompanied by a corresponding decrease in toughness. This is evidenced in the same table by the results of impact tests on samples quenched from 1150° C. followed by holding for one month at the above-mentioned temperatures and then by air-cooling, the samples being tested at room temperature. The steels tested under these conditions retained their toughness to a remarkable degree after the treatments at 400°, 475° and 550° C., although susceptible to disintegration. Holding at the higher temperatures, especially near 750° and 850° C., caused a decrease in toughness, but the steels so treated were not subject to intergranular attack. In fact, 650° C. approximates a border-line temperature with respect to these effects, and this seems especially true when the carbon content is low.

The foregoing evidence indicates that two distinct problems arise in the use of the austenitic chromium-nickel steels at elevated temperatures, although near 650° C. both defects concur and may even intensify each other. The loss in toughness from exposure to the higher temperatures is not so serious, inasmuch as the steels still exhibit Izod values of 40 ft.-lb. or more. Likewise the decrease in corrosion resistance is general rather than localized at the grain boundaries. Hence the extreme desirability of an agent able to inhibit the changes that occur in the lower temperature range, and which initiate attack at the grain boundaries of the metal, even though the steels at the same time may lose toughness when exposed to the higher range.

Fig. 1 illustrates at magnifications of 100 and 2000 diameters the structures of a steel of the 18-8 type containing 0.07 per cent carbon after quenching from 1150° C. and holding at a series of temperatures between 300° and 850° C. The photomicrographs show that when the steel is heated at 400°, 475° and 550° C. finely divided matter is precipitated in the grain boundaries, and accordingly the steel is subject to attack in these

regions. Heating the same steel at 650° C. results in precipitating larger particles at the grain boundaries, but the metal is still susceptible to

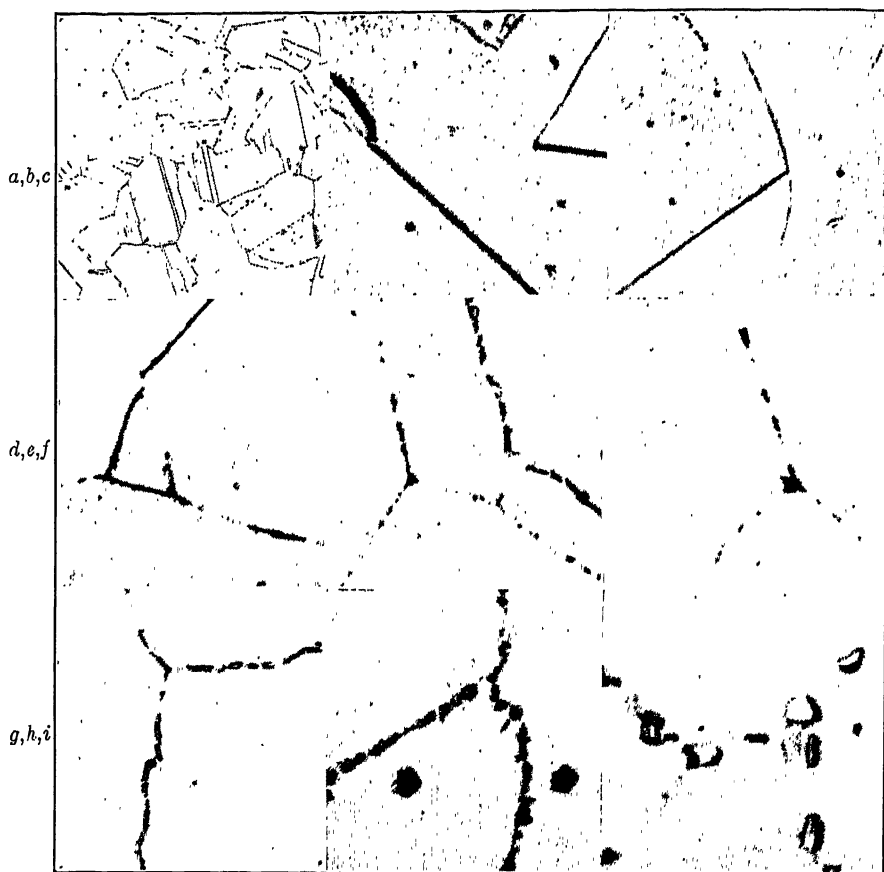


FIG. 1.—EFFECT OF HOLDING AT DIFFERENT TEMPERATURES ON THE STRUCTURE OF THE 18 PER CENT CHROMIUM-8 PER CENT NICKEL STEEL.

- a. 17.50 per cent Cr, 8.88 per cent Ni, 0.07 per cent C. Quenched from 1150° C. $\times 100$.
 b. Same steel quenched from 1150° C. $\times 2000$.
 c. Same as b, held 1 week at 300° C. and air-cooled. $\times 2000$.
 d. Same as b, held 1 week at 400° C. and air-cooled. $\times 2000$.
 e. Same as b, held 1 week at 475° C. and air-cooled. $\times 2000$.
 f. Same as b, held 1 week at 550° C. and air-cooled. $\times 2000$.
 g. Same as b, held 1 week at 650° C. and air-cooled. $\times 2000$.
 h. Same as b, held 1 week at 750° C. and air-cooled. $\times 2000$.
 i. Same as b, held 1 week at 850° C. and air-cooled. $\times 2000$.
 Reduced 25 per cent; original magnification given.

intergranular attack. By advancing the temperature still further to the range of 750° to 900° C., either for a long or short period, the steel is finally rendered immune to this type of attack, and as shown in views *h* and *i* of Fig. 1 the particles in the grain boundaries become considerably

larger. When considered in connection with other data later to be given, the preceding evidence leads the authors strongly to suspect that the precipitates formed at the lower and higher temperatures are not identical in composition.

To acquire additional information concerning the changes that occur on heating at the lower temperatures, critical-point determinations were made on 18-8 chromium-nickel steels, using the procedure standard for ordinary steels. The resulting curves gave no indication of a change in structure. Realizing the extreme sluggishness of the thermal reactions

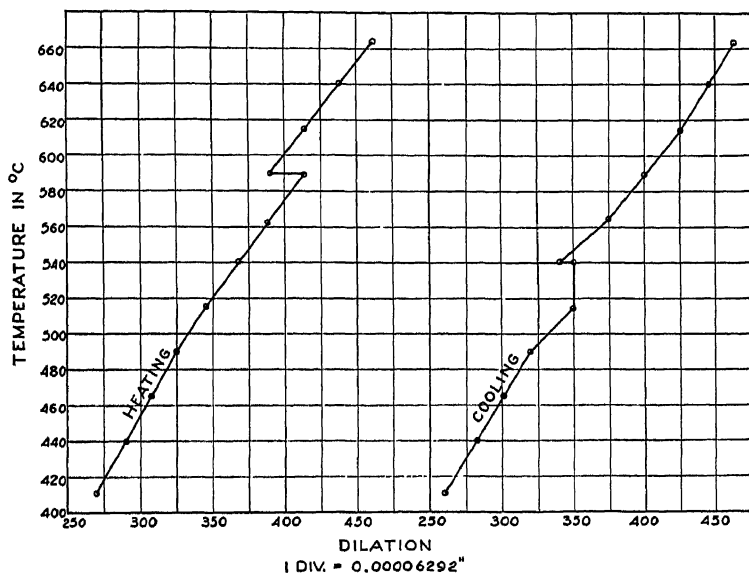


FIG. 2.—CRITICAL-POINT DETERMINATION ON A STEEL CONTAINING 18.45 PER CENT CR, 8.56 PER CENT NI AND 0.12 PER CENT C.

in the austenitic chromium-nickel steels, a modified procedure was introduced to allow sufficient time for structural changes to occur. The plan involved heating the samples in a Rockwell dilatometer to about 400° C. and maintaining this temperature for 24 hr., during which period readings were taken to ascertain when the steel had reached an approximate equilibrium. The reading that denoted this state established the initial point of the curve. At the close of the 24-hr. period the temperature was increased 25° C. and again held for an equal period, and as before dilatometer readings were taken to establish the second point. This procedure was continued until a temperature approximating 650° C. had been reached, whereupon this temperature was maintained for 24 hr. to obtain the final point on the heating curve. Thereupon the samples were cooled at the same rate to provide points for the corresponding cooling curve.

In Fig. 2 are represented the heating and cooling curves for a 0.12 per cent carbon, chromium-nickel steel. On heating, the change which begins at 515° C. ends abruptly at 590° C.; on cooling, the change starts at 565° C. and is completed at 490° C.

Fig. 3 depicts similar data relating to a chromium-nickel steel of 0.07 per cent carbon content, the points having been determined during 48-hr. heating periods. In this instance the changes on heating begin at 425° C. and end at 575° C., whereas on cooling the changes first appear at 575° C. and continue until 450° C. is reached. On heating it should

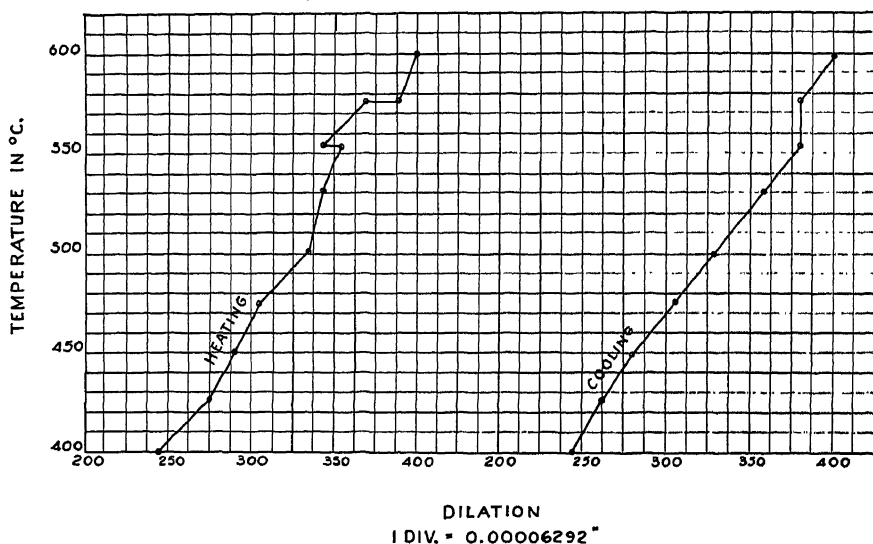


FIG. 3.—CRITICAL-POINT DETERMINATION ON A STEEL CONTAINING 17.47 PER CENT CR, 9.27 PER CENT NI AND 0.07 PER CENT C.

be noted that at 555° C. a decided contraction takes place, whereas an increase of about 25° C. causes appreciable expansion of the metal. Knowing that the 18 per cent-8 per cent chromium-nickel steels are particularly sensitive to intergranular attack at temperatures approximating this range, and bearing in mind the temperature variations under industrial conditions, a detailed investigation within this range might yield valuable information leading to the explanation of intergranular corrosion. It should be understood that some of these changes take place so gradually in the austenitic chromium-nickel steels that definite end points can hardly be found.

In 1929, Dr. H. H. Lester³ showed that at the higher temperatures some of the steels of this class exhibited a critical point at 720° C. on heating, while on cooling a change occurred at about 620° C.

³ H. H. Lester: Paper presented before Amer. Soc. Steel Treat., Cleveland, Ohio, Sept. 13, 1929.

It seems advisable to describe briefly some work of the authors on steels of the 18 per cent-8 per cent chromium-nickel variety containing exceptionally low percentages of carbon. The series ranged from 0.006 to 0.009 per cent in carbon contents. Taking for example a steel that analyzed 19.92 per cent chromium, 8.08 per cent nickel and 0.006 per cent carbon, it should be reported that after applying all the regular tests it was not found possible to induce intergranular corrosion in this steel despite the fact that it had been subjected to 300°, 400°, 475°, 550°, 650°, 750° and 850° C. for varying periods extending to five months, following by boiling for 600 hr. in acidified copper sulfate

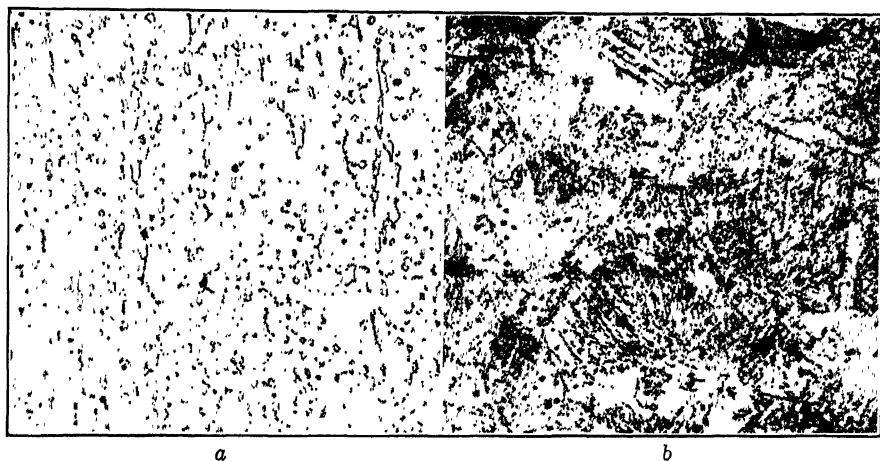


FIG. 4.— STRUCTURE OF 18 PER CENT CHROMIUM-8 PER CENT NICKEL STEELS CONTAINING LESS THAN 0.01 PER CENT CARBON. $\times 250$.
a. 19.88 per cent Cr, 10.14 per cent Ni, 0.008 per cent C. Quenched from 1150° C.
b. 17.10 per cent Cr, 9.12 per cent Ni, 0.009 per cent C. Quenched from 1150° C.

after the treatment at each temperature. The same remarks apply to a steel that contained 18.34 per cent chromium, 10.53 per cent nickel and 0.009 per cent carbon. That these steels were all noticeably magnetic after quenching from 1150° C. is an important point to emphasize. Fig. 4 shows the structures of two of these steels containing respectively 0.008 and 0.009 per cent carbon. Steel *b* could not be disintegrated under the treatments described above; on the other hand, steel *a* showed slight signs of grain-boundary attack after holding for two months at 400° and 475° C. followed by boiling for 100 hr. in the copper sulfate solution. Explanation might well be asked of the difference in the resistance to intergranular attack of steels having analyses so nearly the same, and both so low in carbon. The authors have no explanation, and only a suggestion is offered that the ratio of chromium to nickel may exercise an important influence even in steels so low in carbon.

It has been stated in this paper that the addition of columbium to the austenitic chromium-nickel steels led to exceedingly satisfactory results. In Table 2 it should be observed that the presence of approximately four times as much columbium as carbon diminished the range of temperature through which these steels were attacked at the grain boundaries. When the ratio of columbium to carbon was increased to about seven to one, a marked improvement was obtained, although it was still possible to disintegrate the steel. Further increase of columbium to at least 10 times the carbon yielded steels that failed to disintegrate after exposure for either long or short periods at all the temperatures between 300° and 850° C. As expected, steels containing even higher ratios of columbium

TABLE 2.—*Corrosion Tests on Chromium-nickel Steels Containing Columbium*

(All samples quenched from 1150° C. before testing)

Cr,° Per Cent	Ni, Per Cent	Cb, Per Cent	C, Per Cent	Approximate Temperatures Within Range 300°-850° C. that Cause Subsequent Disintegration in Boiling Acidified Copper Sulfate, Deg. C.
18.39	8.39	0.37	0.14	475 to 650
18.49	8.56	0.44	0.10	550 to 650
18.28	9.42	0.51	0.07	550
18.36	9.38	0.79	0.13	650
18.33	9.16	1.51	0.18	550
18.75	9.02	1.00	0.11	650
17.81	9.18	0.75	0.07	None found
18.63	9.27	1.25	0.12	None found
18.75	9.14	2.13	0.12	None found
22.87	12.43	1.50	0.14	None found
26.06	20.44	1.51	0.14	None found

* These steels also contained normal amounts of manganese, silicon, phosphorus and sulfur.

to carbon also resisted disintegration. However, except in connection with very low carbon, columbium does not greatly correct the loss of toughness characteristic of exposure in the approximate range of 650° to 900° C.

Seeking better understanding of the action of columbium, a long-time critical-point determination was made on a steel containing 1.16 per cent columbium and 0.10 per cent carbon, using the modified procedure earlier described. The results shown in Fig. 5 reveal that the changes which occur in the ordinary chromium-nickel steels are entirely absent, the columbium-bearing steel having expanded and contracted normally on heating and cooling. Is it not probable that the substantial elimination of these changes explains at least in part the efficacy of columbium in inhibiting intergranular corrosion?

The results of physical and corrosion tests on a series of columbium-bearing steels are of interest. It may be observed from Table 3 that fully softened steels containing up to about 2 per cent columbium

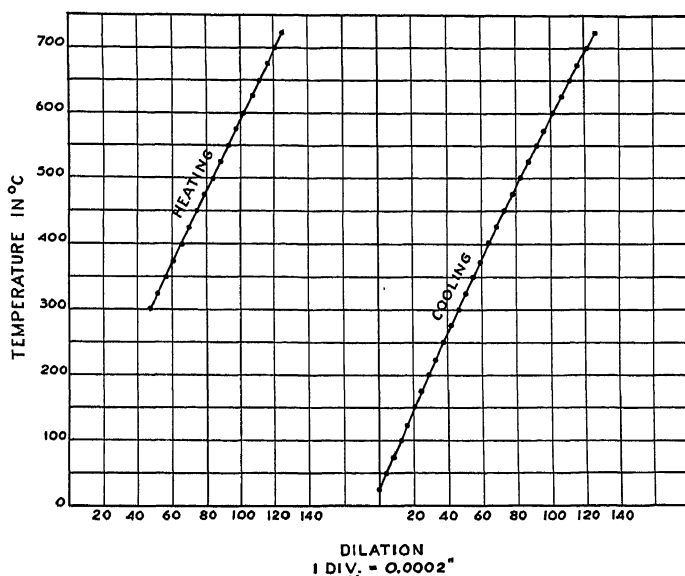


FIG. 5.—CRITICAL-POINT DETERMINATION ON A STEEL CONTAINING 18.38 PER CENT CR, 8.97 PER CENT NI, 1.16 PER CENT CB AND 0.10 PER CENT C.

possess good physical characteristics. The same steels exhibited excellent resistance in the salt-spray test during an exposure of 750 hr.; equally satisfactory results were obtained in boiling 65 per cent nitric acid.

TABLE 3.—*Physical Tests on Chromium-nickel Steels Containing Columbium*

Cr, ^a Per Cent	Ni, Per Cent	Cb, Per Cent	C, Per Cent	Condition of Metal	Yield Point, Lb. per Sq. In.	Max. Stress, Lb. per Sq. In.	Elonga- tion, Per Cent in 2 In.	Reduc- tion of Area, Per Cent	Isod Im- pact, Ft.-lb.	Brinell Hard- ness ^b
18.28	9.42	0.51	0.07	Quenched from 1150° C.	36,000	89,500	60	72	120	137
17.81	9.18	0.75	0.07	Quenched from 1150° C.	35,000	91,700	59	67	120	143
18.63	9.27	1.25	0.12	Quenched from 1150° C.	35,000	91,700	58	66	103	143
18.63	9.27	1.25	0.12	Air-cooled from 1150° C.	41,000	92,750	57	64	102	146
18.52	9.00	2.13	0.15	Quenched from 1150° C.	41,000	91,200	51	64	94	163
18.52	9.00	2.13	0.15	Air-cooled from 1150° C.	36,000	89,500	51	63	98	153
22.87	12.43	1.50	0.14	Quenched from 1150° C.	55,500	91,000	42	58	97	146
22.87	12.43	1.50	0.14	Air-cooled from 1150° C.	52,000	91,000	47	64	98	149
25.06	20.44	1.51	0.14	Quenched from 1150° C.	48,000	90,500	44	63	86	146

^a These steels also contained normal amounts of manganese, silicon, phosphorus and sulfur.

^b 3000-kg. weight.

Chromium-nickel steels containing columbium in the proper ratio to carbon are well adapted to welding by either the oxyacetylene or the arc method. Table 4 shows the results of tests on welded $\frac{3}{16}$ -in. plates, using rods of the same analysis, and it may be observed that welds with markedly improved resistance to corrosion in both the weld and the adjacent zones are obtainable. In the welded state protection from localized failure in the weld or adjacent zone is obtained when columbium reaches substantially four to five times the content of carbon, provided the carbon does not exceed 0.10 per cent. This statement applies to

TABLE 4.—*Corrosion Tests on Welds Made in $\frac{3}{16}$ -in. Columbium-treated Chromium-nickel Steel Plate*

Composition of Plate and Rod, Per Cent				Method of Welding ^a	Penetration per Month in Boiling 65 Per Cent HNO ₃ , In. 240-hr. Tests	Remarks
Cr	Ni	C	Cb			
18.49	8.56	0.10	0.44	Oxyacetylene	0.0022	No noticeable attack in welds or adjacent zones.
18.49	8.56	0.10	0.44	Arc	0.0014	No noticeable attack in welds or adjacent zones.
17.59	8.05	0.16	0.71	Oxyacetylene	0.0087	Noticeable attack in welds and adjacent zones.
17.59	8.05	0.16	0.71	Arc	0.0061	Noticeable attack in welds and adjacent zones.
18.26	9.38	0.13	0.79	Oxyacetylene	0.0028	No noticeable attack in welds or adjacent zones.
18.26	9.38	0.13	0.79	Arc	0.0023	No noticeable attack in welds or adjacent zones.
18.75	9.02	0.10	1.00	Oxyacetylene	0.0014	No noticeable attack in welds or adjacent zones.
18.75	9.02	0.10	1.00	Arc	0.0015	No noticeable attack in welds or adjacent zones.

^a Previous to welding the plate was air-cooled from 1150° C. The samples tested were 4 in. long and 1 in. wide.

welds made by either process in plate having a maximum thickness of $\frac{3}{16}$ in. When the carbon approximates 0.13 per cent, a columbium to carbon ratio of six or seven to one is required. The fact that little columbium is lost during welding doubtless has a favorable influence on the results. Fig. 6 relates to welding and probably holds much interest.

While these data show little difference in the corrosion resistance of welds whether made by the oxyacetylene or the arc process, provided the steel has the proper ratio of columbium to carbon, it must be emphasized that good welding technique is required. However, these statements refer only to welds that are required to resist corrosion at room temperature or slightly above. If they must withstand corrosion associated

with high temperatures, both rod and plate should contain at least 10 times as much columbium as carbon.

The satisfactory experimental results from columbium in the small heats leading to ingots 2 by 2 in. in section have been duplicated in the production of 8 by 8-in. ingots. The alloying addition is made with



FIG. 6.—EFFECT OF COLUMBIUM ON CORROSION RESISTANCE OF WELDS MADE IN 12-GAGE LOW-CARBON 18 PER CENT CHROMIUM-8 PER CENT NICKEL STEEL SHEET.

a. 0.06 per cent carbon, chromium-nickel steel sheet welded by oxyacetylene process, followed by test in a nitric-hydrofluoric acid solution.

b. 0.06 per cent carbon, chromium-nickel steel sheet containing 0.67 per cent columbium welded by oxyacetylene process, followed by test in same solution.

c. 0.06 per cent carbon, chromium-nickel steel sheet welded by arc process, followed by test in same solution.

d. 0.06 per cent carbon, chromium-nickel steel sheet containing 0.67 per cent columbium welded by arc process, followed by test in same solution.

ferrocolumbium containing from 50 to 60 per cent columbium and of low carbon content. By adding the alloy through the slag to a thoroughly deoxidized steel just before pouring, allowing sufficient time however for the columbium to alloy with the melt, recoveries of 80 to 90 per cent of the columbium can be secured in the finished steel. From the larger ingots these columbium-bearing steels have been fabricated under normal conditions in a commercial mill into rods, bars, plates, sheets and strips, and billets have been pierced and drawn to seamless tubes.

Initial hot-working temperatures of these steels should not greatly exceed 1200° C. The procedures usual to the annealing and pickling of the plain 18 per cent-8 per cent chromium-nickel steels are suitable for those containing columbium.

TABLE 5.—*Physical and Corrosion Tests on Chromium-nickel Steel Containing Columbium Rolled in Commercial Mill*

	Composition, Per Cent			
	Heat N-27		Heat N-19	
Chromium.....	18.39		18.38	
Nickel.....	8.95		8.97	
Silicon.....	0.37		0.63	
Manganese.....	0.54		0.68	
Carbon.....	0.06		0.10	
Columbium.....	0.67		1.16	

Condition of Metal	Quenched from 1150° C.	Air-cooled from 1150° C.	Quenched from 1150° C.	Air-cooled from 1150° C.
Yield point, lb. per sq. in.....	37,000	36,000	38,800	39,000
Maximum stress, lb. per sq. in..	89,000	87,000	89,500	91,500
Elongation, per cent in 2 in.....	57	59	56	55
Reduction of area, per cent.....	68	69	70	68
Izod impact, ft-lb.....	117	104	101	108
Brinell hardness.....	131	131	143	140
Penetration per month in boiling 65 per cent HNO ₃ , in. Five 48-hr. periods.....	0.0011		0.0024	
Results of salt-spray tests (20 per cent sodium chloride solu- tion).	Unaffected in 500 hr.	Unaffected in 500 hr.	Unaffected in 500 hr.	Unaffected in 500 hr.

In Table 5 appear the results of tests on commercially rolled columbium-bearing steels both medium and low in carbon. Again it is to be noted that the steels have excellent physical characteristics and satisfactorily meet the salt-spray and nitric acid tests.

Fig. 7 shows photomicrographs of the steels described in Table 5, views *a* and *b* representing the unetched condition. Both steels are relatively free from inclusions, a condition characteristic of substantially all the columbium-bearing steels produced during this investigation. For the lower carbon steel (0.06 per cent C) the structure is also shown, and in Fig. 7c it is apparent that this steel has an austenitic structure consisting of small grains, which refinement of structure is usually imparted by columbium. However, if the columbium content is increased to about 1.25 per cent or higher, the metal will contain small quantities of ferrite in addition to austenite and carbides. After quenching from

1150° C., the samples of the lower carbon steel were held respectively at 300°, 400°, 475°, 550° and 650° C., and the photomicrographs reveal

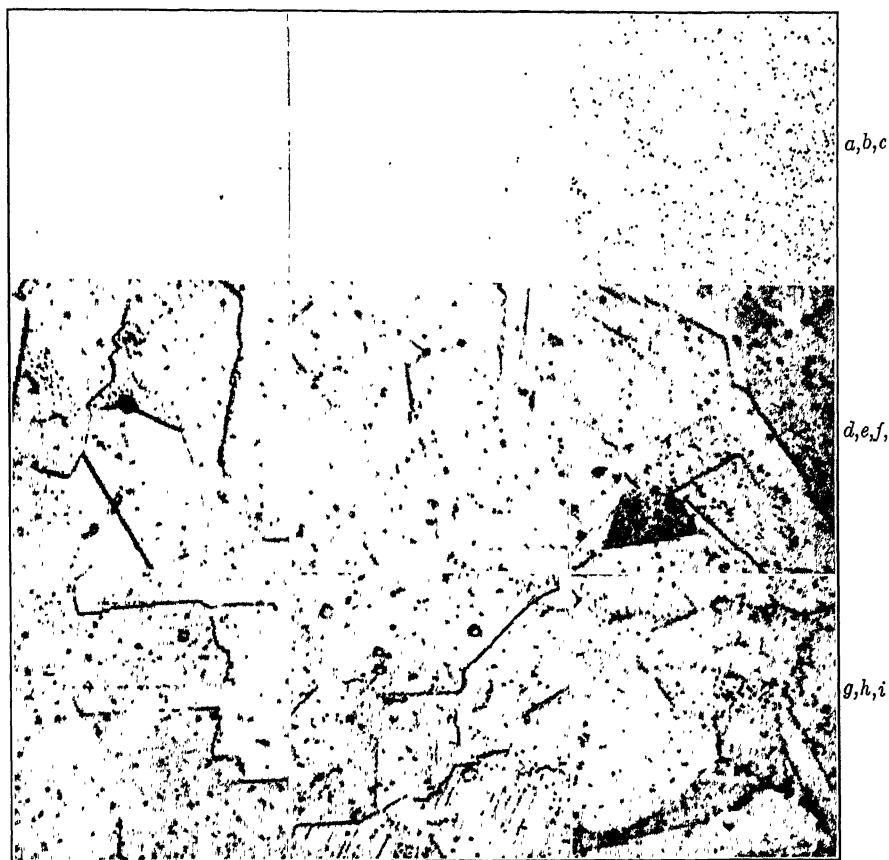


FIG. 7.—EFFECT OF HOLDING AT DIFFERENT TEMPERATURES ON THE STRUCTURE OF THE COLUMBIUM-TREATED 18 PER CENT CHROMIUM-8 PER CENT NICKEL STEEL.

a. 18.39 per cent Cr, 8.95 per cent Ni, 0.06 per cent C, 0.67 per cent Cb. Unetched. $\times 100$.

b. 18.38 per cent Cr, 8.97 per cent Ni, 0.10 per cent C, 1.16 per cent Cb. Unetched. $\times 100$.

c. 18.39 per cent Cr, 8.95 per cent Ni, 0.06 per cent C, 0.67 per cent Cb. Quenched from 1150° C. $\times 100$.

d. Steel c quenched from 1150° C. $\times 2000$.

e. Same as d, held 1 week at 300° C. and air-cooled. $\times 2000$.

f. Same as d, held 1 week at 400° C. and air-cooled. $\times 2000$.

g. Same as d, held 1 week at 475° C. and air-cooled. $\times 2000$.

h. Same as d, held 1 week at 550° C. and air-cooled. $\times 2000$.

i. Same as d, held 1 week at 650° C. and air-cooled. $\times 2000$.

Reduced 25 per cent; original magnification given.

the absence of the precipitation so apparent at the grain boundaries of plain 18 per cent chromium-8 per cent nickel steels similarly treated

(Fig. 1). This striking difference is firmly believed to explain the effectiveness of columbium in inhibiting attack at the grain boundaries.

It seems entirely fair to conclude that the addition of columbium in moderate and economical proportions inhibits intergranular deterioration of the austenitic chromium-nickel steels when exposed concurrently to elevated temperatures and chemical corrosion. This enhancement of corrosion resistance does not require sacrifice of the present valuable properties. Susceptibility to intergranular corrosion has limited use of these steels in logical fields, and the proffered remedy of this defect is expected to give fresh impetus to industrial utilization.

ACKNOWLEDGMENT

The thanks of the authors for enthusiastic cooperation are tendered several staff members of Union Carbide and Carbon Research Laboratories, Inc.: Mr. James Thompson and Mr. W. L. Harbrecht for the making of steel ingots; Mr. T. R. Cunningham and Mr. R. J. Price for special chemical analysis; Mr. J. R. Vilella for metallographic examination; Mr. F. E. Bacon and Mr. C. R. Bishop for corrosion testing; and Mr. W. B. Miller and Mr. A. R. Lytle for the data related to welding.

DISCUSSION

(Jerome Strauss presiding)

O. E. HARDER,* Columbus, Ohio (written discussion).— Among the many valuable contributions contained in this paper it appears to me that one of the most interesting is the rather convincing proof that susceptibility to intergranular corrosion and loss in toughness after heating at certain elevated temperatures are two different phenomena. The authors have quite clearly shown that in many instances recovery from susceptibility to corrosion disintegration is obtained at about the temperature at which the loss in ductility begins.

The susceptibility to intergranular corrosion may be assumed to be explainable on the basis of the theories that have already been advanced. The loss of impact resistance upon heating in the range of 550° to 850° C. does not seem to be explainable on the basis of theories that have been advanced, if it is assumed, as seems to be established in the present research, that susceptibility to intergranular corrosion and loss in impact value are not due to the same cause.

Before proposing a possible mechanism for this loss in impact value, I wish to comment upon the dilation curves reported in this paper. At first thought one might attempt to account for the contraction on heating and expansion on cooling by solution and precipitation respectively. However, if we assume that the carbide solubility curve is at least approximately that published by Bain, Aborn, and Rutherford,⁴ it seems unlikely that any detectable solution would take place at a temperature as low as 600° C. Furthermore, solution of carbides according to their diagram should take place over a considerable range of temperature rather than at a fairly well defined temperature. Agglomeration of a precipitated phase might cause some contraction,

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⁴ Reference of footnote 2.

but again this should take place gradually over a range of temperature and would provide no mechanism for expansion on cooling. Reference to the structural diagram for carbon-free alloys with 18 per cent chromium and variable amounts of nickel as drawn by Krivobok⁵ and to the diagram by the same author showing the effect of carbon on the trend of reactions in 18 per cent chromium—8 per cent nickel steels may suggest an explanation for the observed critical points on heating and cooling. In the carbon-free alloys with 8 per cent nickel the boundary between the alpha plus gamma and the gamma fields is at about 560° C. With 18 per cent chromium, 8 per cent nickel and 0.1 per cent carbon the boundary is at just above 500° C. These temperatures are in quite good agreement with critical temperatures of 515° to 590° C. and 425° to 575° C. reported in the present research. It so happens that the alloy of lower carbon content was higher in nickel, and these variations in carbon and nickel contents would tend to compensate each other. Does not the possible presence of a small amount of ferrite in these alloys, which is either present at ordinary temperatures or is formed on heating and later transforms to austenite on further heating and then changed back to ferrite on slow cooling, provide a plausible mechanism for the observed critical points?

Now to return to the loss in impact values upon heating within the range of 550° to 850° C. It must be remembered that the authors air-cooled all specimens from the various reheating temperatures. Presumably 20-gage sheet would be air-quenched and thus might not form ferrite. On the other hand, Izod specimens are larger, and air-cooling would be slower and might result in the formation of at least traces of ferrite and thus cause loss in ductility due to internal stress. In Table 1 the higher the carbon content, the lower the reheating temperature required to lower the impact value. Perhaps the authors have unpublished data that will support or deny the above suggestions. If these suggested mechanisms are found to hold, the absence of critical points in the heating and cooling curves of the columbium-treated steel must be attributed to the absence or differences in the character of the ferrite rather than to the character of the carbides, although the phenomena may be related.

With regard to the amount of columbium (or titanium) required in steels of different carbon content, might it not be better to assume a certain carbon solubility, say 0.02 per cent, and calculate the amount of the "carbon-fixing" metal on the basis of the excess carbon?

While this paper shows the effective use of columbium in preventing intergranular corrosion and in an earlier paper Bain and associates⁶ have demonstrated the effectiveness of titanium for a similar purpose, I wonder if the possibilities of heat-treating these austenitic chromium-nickel steels as a means of preventing intergranular corrosion have been exhausted. To suggest a heat treatment based on a metallurgical "hunch" without having supporting experimental evidence may be a dangerous procedure. There appears, however, to be one rather feasible way of attempting to stabilize these steels, which does not seem to have been tried so far as published information has come to my attention.

This heat treatment would consist of rapidly cooling the steels from the usual quenching temperatures, about 2000° F., to a temperature of maximum rate of carbide precipitation, probably about 1000° to 1200° F., holding the steels at this temperature until precipitation is completed or nearly so, followed by reheating to a somewhat higher temperature in order to effect some growth or agglomeration of the precipitated carbide, probably at a temperature of about 1400° F. Davenport and Bain⁷ have

⁵ V. N. Krivobok: *The Book of Stainless Steels*, 19-49. 1933.

⁶ Reference of footnote 2.

⁷ E. S. Davenport and E. C. Bain: *Transformations of Austenite at Constant Subcritical Temperatures*. *Trans. A.I.M.E.* (1930) 90, 117-144.

clearly shown that there is a temperature range of maximum rate of formation of pearlite from austenite and that there is another range of maximum rate of formation of martensite from austenite in plain carbon and slightly alloyed steels. It is appreciated that the precipitation of carbide may be a somewhat different phenomenon, and yet it seems reasonable to assume that there is a temperature range in which precipitation takes place rapidly. It is indicated by reheating experiments that there are temperature ranges in which precipitation takes place more rapidly than in others. It is expected that if precipitation can be made to take place very rapidly the carbide particles will be precipitated throughout the structure with little or no concentration at the grain boundaries.

The reheating to the somewhat higher temperature proposed would have for its purpose increasing the size of the carbide particles and thus increasing their stability, but it is obvious that this reheating temperature will have limitations, because if carried too high resolution of the carbide particles would take place and might result in grain-boundary precipitation due to future heating at a somewhat lower temperature. It is known that reheating to temperatures of 1550° to 1650° F. after quenching for stabilization has been proposed and used with some success.⁸ Likewise, working the steel down to relatively low temperatures, about 1550° F., has been used to effect some stabilization.

A very limited amount of work has been done on this suggested heat treatment, but the results are entirely too meager to justify their presentation in its support. Metallurgists familiar with stainless steel, with whom this heat treatment has been discussed, consider it sound metallurgically but are doubtful regarding its practicability.

P. PAYSON,* Harrison, N. J. (written discussion).—This paper is a welcome addition to the literature on the effects of low-temperature heating on the austenitic stainless steels, first because it introduces a new method of preventing intergranular corrosion, and second because it points out that the heating conditions, and hence the structural conditions, that bring about decreased resistance to intergranular corrosion are not necessarily the same as those that bring about decreased impact resistance. This implies that the causes for these effects are not the same, and that a cure for one of these troubles may not be a cure for the other. I agree with the authors that the precipitate that causes susceptibility to intergranular corrosion is probably of a different composition from that which causes decreased impact toughness. But there is another effect of heating these steels at these temperatures which is not mentioned in the paper—that steels that may be resistant to intergranular corrosion, as measured in the acid CuSO_4 solution after long heating at these temperatures, may at the same time be very poorly resistant to general over-all corrosion as determined, for example, in the boiling nitric acid test. It would be interesting to know whether the authors made nitric acid tests on some of their samples which had been held for a long time at the intermediate temperatures.

Enough time has now elapsed since the discovery of intergranular corrosion in these steels to make us realize that this defect of the austenitic steels has been very much overemphasized. In 1930 many people began to fear that some of their expensive installations would soon come crumbling down because of intergranular corrosion. Practically all of these are still probably as sound today as they were then, and will continue to be so for many more years. I have encountered some cases where failure was undoubtedly due to intergranular corrosion, but there have also been many cases where intergranular corrosion was suspected but where the failure was due to some entirely different cause.

⁸ Reference of footnote 2.

* Crucible Steel Company of America.

The overemphasis on this subject in the literature has probably intimidated many possible consumers of 18-8 into buying the more expensive modified compositions when ordinary 18-8 with 0.08 C maximum might have been perfectly satisfactory for their purpose. The service conditions that combine long-time heating at intermediate temperatures with exposure to active electrolytes are very rare, yet many investigators, including the present authors, have heated their samples for hundreds of hours before subjecting them to the boiling acid copper sulfate test, which in itself is a much more severe condition than a great many installations are subject to.

The very striking effect of the nitric-hydrofluoric reagent on welded samples, as shown in Fig. 6, is another form of overemphasis. Indeed, this test may be very misleading, as shown by some results which we have just obtained. Four steels with 17.5 to 19.5 Cr, 8.6 to 9.6 Ni and 0.06 to 0.10 C, were annealed at 1900° and were then arc-welded. The welded samples were tested in the acid copper sulfate solution for about 200 hr., in the boiling 65 per cent nitric acid solution for two 48-hr. periods and in the nitric-hydrofluoric acid solution for 2 hr. The orders of merit in the three tests were as follows:

Per Cent Carbon	Acid CuSO ₄	65 Per Cent HNO ₃ , In. per Month	HNO ₃ -HF
0.06	No attack	0.0015	Third best
0.07	Very slight attack	0.0013	Worst attack
0.08	Severe attack	0.0017	Second best
0.10	Severe attack	0.0027	Least attack

In spite of the fact that 0.06 C steel looked bad in the nitric-hydrofluoric test, I would feel safe in recommending the use of 18-8 steel with 0.06 C for welded tanks which were not to be annealed after welding and which were to be used in contact with boiling nitric acid.

I do not wish to minimize the seriousness of intergranular corrosion under certain conditions, but I do believe it should be made clear that only relatively few conditions of service require the highly resistant modified compositions of 18-8. For such conditions the columbium steel should be highly satisfactory.

R. H. ABORN,* Kearny, N. J. (written discussion).—It is clearly evident that columbium as well as titanium may provide an entirely effective means of inhibiting intergranular corrosion without altering the inherently valuable properties of the austenitic structure. In all probability, they function alike, through their strong carbide-forming properties, to tie up the carbon and thereby prevent insidious chromium depletion. For certain purposes, such as welding rod, the columbium-bearing material possesses some advantages (owing to lower oxidation of the added element in melting) but for most purposes we are inclined to believe that both types possess approximately equal value.

The authors declare that the "procedures usual to the annealing of plain 18-8 steels are suitable for those containing columbium." It is our experience, however, that annealing at some 1100° C., which is not uncommon for regular 18-8, may deleteriously affect the intergranular-corrosion resistance of the columbium product as judged by systematic thermal-gradient sensitization tests; and that a stabilizing heat treatment at 800° to 900° C., designed to achieve maximum tying up of the carbon content, improves the columbium-bearing steel precisely as it improves the titanium product.

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It is suggested that the observed irregularities in the dilation-temperature curves of the regular 18-8 alloys are occasioned by the transformation of some austenite to ferrite incident to the precipitation of chromium-rich carbide. In itself this transformation of some austenite to ferrite incident to the precipitation of chromium-rich carbide. In itself this transformation is probably of little practical significance and would vanish with a sufficiently high ratio of nickel to chromium.

In view of the close similarity in chemical properties between columbium and tantalum, it would be interesting to know whether the authors have investigated tantalum-bearing alloys and whether or not appreciable quantities of tantalum may be found in the columbium-bearing product.

With regard to Dr. Harder's proposed method of stabilizing the plain 18-8 alloy, I might add that such a method has been worked out successfully and is fully described in a paper by Bain, Aborn and Rutherford.⁹

P. PAYSON.—Some time ago we were working on three steels that were about 0.08 to 0.20 carbon, and we tried the effect of stabilizing at a high temperature, around 1600° to 1650° F., with the same idea that Dr. Harder offered, of precipitating all the carbon and agglomerating it to a large size where it would no longer have any effect. We found that by reheating for 10 min. at 1200° F. after about 6 hr. at 1600° F. we again made the material susceptible to intergranular corrosion, which is something I cannot explain.

I thought that by heating first for a long time at the temperature where the harmful precipitation occurs, say around 1100° to 1200° F., and then heating at a higher temperature for a long time, we could have a better chance for complete agglomeration of the carbides. This procedure showed some promise but was not altogether successful. We heated for longer and longer periods of time at 1450°, and eventually we did get resistance to intergranular attack after a comparatively short time heating at 1200°, but the time required at 1450° was about a week, and that put it outside the class of practical heat treatment. A very surprising thing happened; the 0.20 carbon steel was more readily stabilized than the 0.08 carbon steel, which is another thing that is difficult to explain.

H. W. GILLET,* Columbus, Ohio.—Is there sufficient columbium for commercial use?

R. FRANKS.—We feel sure there will be sufficient columbium for use in steels required to resist intergranular corrosion.

Mr. Payson's question regarding nitric acid tests is pertinent. We actually held a series of samples, both the plain chromium-nickel steels and the columbium-treated chromium-nickel steels at all of the temperatures between about 300° and 900° C. The steels were held at temperature for a period of about one week after they were given five 48-hr. boiling periods in concentrated nitric acid. The columbium-treated steel was seriously attacked only after treatment at one temperature. I believe this temperature was in the neighborhood of 550° C. The plain chromium-nickel steels were very badly attacked after heating between 475° and 700° C. However, after treatment at 850° C. the plain chromium-nickel steels were almost as resistant as they were after quenching from the annealing temperature.

Mr. Payson also made statements concerning the severity of the tests that consisted of holding the steels for longer periods at high temperature previous to boiling in copper sulfate. Of course, even with 0.06 carbon intergranular corrosion develops after a few hours at 500° to 600° C. if the steel is boiled in acid copper sulfate or nitric acid.

⁹ Reference of footnote 2.

* Director, Battelle Memorial Institute.

Dr. Aborn states that it is necessary to use a stabilizing treatment on the columbium-treated chromium-nickel steels. It has been our experience that for practical purposes it is unnecessary to employ such a heat treatment, if enough columbium is present in the steel. As a matter of fact, we found early in our work that quenching a steel from, say, 1150° C., rendered it far more susceptible to intergranular attack than air-cooling. Therefore, in all of our work we used a quench from 1150° C. on samples that were subsequently subjected to all the temperatures between 300° and 900° C.

We made just as many experiments with tantalum as we did with columbium, and we found that a similar result could be secured with tantalum in low-carbon steels. By "similar result," I mean that with a 0.06 or 0.07 carbon steel it is necessary to have present about 2 to 2.25 per cent of tantalum to impart relative freedom from intergranular attack.

In higher carbon steels, for example 0.10 or 0.12 per cent carbon, around 3 to 4 per cent tantalum is required. In addition, this larger amount of tantalum actually decreases the ductility of the steels slightly. However, the high-tantalum steels did exhibit good elongation values. These steels gave values in the neighborhood of 40 per cent elongation after annealing, showing that they were not as satisfactory in this respect as the plain chromium-nickel steels and also the columbium-treated chromium-nickel steels.

It is true that all of the ferrocolumbium alloys we have made contain a few per cent of tantalum. The alloys contain something like 2 to 5 per cent of tantalum and 55 to 60 per cent columbium. A method has been developed at the laboratory for determining both the columbium and the tantalum content of these steels.

F. M. BECKETT and R. FRANKS (written discussion).—Dr. Harder is correct in stating that the data presented indicate that the loss of impact resistance upon heating in the range of 550° to 850° C. cannot be explained by the theories advanced to account for the development of intergranular corrosion in the austenitic chromium-nickel steels. It has been our experience that the higher carbon steels begin to lose toughness at lower temperatures than those containing less carbon, because the higher carbon steels are inherently less stable. We believe the quenching of these steels from sufficiently high temperature gives a solid solution of the iron, chromium and nickel more nearly saturated with carbides, and that on subsequent heating the constituent causing loss of toughness forms at a lower temperature.

Dr. Harder's comments relating to the use of a heat treatment to coagulate carbides to inhibit intergranular corrosion are pertinent. Considerable experimentation was carried on several years ago at our laboratories with this idea in mind, but the process required such long heating periods to secure anything like the desired improvement that it did not indicate commercial feasibility. We do not believe Dr. Harder's suggested heat treatment, consisting of first quenching the steels from about 2000° F. and cooling them sufficiently slowly to 1000° to 1200° F. to cause maximum carbide precipitation, followed by reheating to a somewhat higher temperature, for example 1400° F., would yield a satisfactory increase in resistance to intergranular attack.

The authors cannot fully agree with Dr. Aborn's statements concerning the necessity of using a stabilizing heat treatment at 800° to 900° C. after annealing the columbium-bearing steels at 1100° C., to achieve suitable resistance to intergranular corrosion. Numerous tests have shown that if sufficient columbium is present in the chromium-nickel steels it is unnecessary from a practical standpoint to use such a stabilizing heat treatment. However, it is possible to employ such a treatment economically if the steel in question contains too little columbium to impart the desired characteristics. As stated in the paper, approximately 10 times

as much columbium as carbon is needed to obtain satisfactory results under all conditions. If the columbium to carbon ratio is in the vicinity of 7:1 or even lower, we appreciate that resistance to intergranular corrosion can be greatly improved by the use of a stabilizing treatment. Experiments conducted at our laboratories some time ago actually gave these results.

Dr. Aborn's point in reference to the effect of tantalum in retarding intergranular corrosion in the chromium-nickel steels is well taken. A considerable amount of testing was done on steels containing various percentages of tantalum in relation to carbon content. In fact, the experiments were made on steels containing various percentages of tantalum and substantially no columbium, tantalum metal having been employed as the addition agent. The results showed that if sufficient tantalum were present the steel would possess remarkable freedom from attack at the grain boundaries. Nevertheless, it required approximately twice as much tantalum as columbium to accomplish this result, which in the instance of high-carbon steels would require a relatively large addition of tantalum. On the other hand, with low-carbon steels it may be possible to use tantalum advantageously for this purpose. The ferroalloys employed in the present work contained between 50 and 60 per cent columbium and between 2 and 5 per cent tantalum.

Mr. Payson brings out an important point in the first part of his discussion. This relates to the decreased general corrosion resistance caused by heating the austenitic chromium-nickel steels at certain temperatures without necessarily inducing intergranular corrosion as measured by the acidified copper sulfate test. We presume that he has in mind some temperature between about 400° and 750° C. A series of tests was conducted in boiling nitric acid on chromium-nickel steel samples, with and without columbium, that previously had been held at these temperatures. The results showed that even under these conditions the columbium-bearing steels were markedly superior to the plain chromium-nickel steels, although they did not maintain fully the resistance they possessed in the annealed state. Similar tests were conducted on other steels containing some of the well-known additions to the chromium-nickel steels to inhibit the development of intergranular corrosion, and again it was noted that the columbium was outstanding in this respect.

Mr. Payson states that the overemphasis placed on the susceptibility of the chromium-nickel steels to intergranular corrosion has perhaps intimidated many possible consumers of the 18-8 steel. He is probably correct in this statement, but we believe he will agree that unless some means is provided for overcoming this difficulty the general use of the 18-8 steel will always be unduly limited.

The data given by Mr. Payson regarding the use of the nitric-hydrofluoric solution in testing welds made in the 18-8 steel agree generally with the results of tests made in our laboratories. This is especially true if the steel in question is unbalanced with respect to nickel, chromium and carbon. Our experience has been that with low carbon content it is important to have the nickel content in the vicinity of 9 per cent or slightly higher with a chromium content of at least 18 per cent. In this table, under the copper sulfate tests, no attack is recorded with a 0.06 per cent carbon steel, while with a 0.07 per cent carbon steel slight impairment was noticeable in the welded sections. We believe that some other factor was responsible for these results rather than the slight difference in carbon content.

An X-ray Study of the Diffusion of Chromium into Iron*

BY LAURENCE C. HICKS,† BRACKENRIDGE, PA.

(Detroit Meeting, October, 1933)

CONSIDERATION of the past work on the subject of the diffusion of chromium into iron suggested that additional information might be given by the use of X-ray spectroscopy in following the concentration changes through the diffusion zone.

Grübe and Fleischbein¹ packed rods of electrolytic iron in a mixture of alumina and chromium. These specimens were heated in an atmosphere of purified hydrogen for varying lengths of time. After treatment the specimens were examined metallographically and showed the usual structure, consisting of a border of radially oriented columnar grains ending in a sharp boundary line. Reference is made to the fact that etching with certain reagents will attack only the material inside the border of columnar growth and also to the fact that polishing seems to develop a ridge at the position of the boundary between the etched and unetched areas. By chemical analysis of thin layers turned off on a precision lathe, the authors were able to obtain depth-concentration curves. These curves, reproduced in Fig. 1, show that in most cases a pronounced change of slope occurs, corresponding to the position of the boundary of the columnar grains.

In a later paper Grübe extends his work to other systems which show the same characteristics.² He concludes that the reason for the break in the curve is that a hindrance of diffusion occurs at the place where the regularly oriented grains of the diffusion zone meet the random grains of the interior portion, on the assumption that the diffusion velocity in one direction in a grain may be greater than in another direction, and that the grains in the diffusion zone orient themselves so as to give the maximum diffusion rate. Kelley³ points out that Grübe has failed to note that the boundary line does not consistently cross all grains and

* A condensation of a thesis submitted in partial fulfillment of the requirement for the degree of Doctor of Science from the Massachusetts Institute of Technology, June, 1933.

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¹ G. Grübe and W. v. Fleischbein: Die Oberflächenveredelung der Metalle durch Diffusion. *Ztsch. f. anorg. u. all. Chem.* (1926) **154**, 314.

² G. Grübe: Die Oberflächenveredelung von Metallen durch Diffusion. *Ztsch. f. Metallkunde* (1927) **19**, 438.

³ F. C. Kelley: Grain Growth in Metals Caused by Diffusion. *Trans. A.I.M.E.* (1928) **78**, Inst. Met. Div., 390.

explains this phenomenon by suggesting that where the boundary line does not occur the interior grain had the same orientation as that assumed by the columnar grain.

Bannister and Jones⁴ in a consideration of the materials employed by other investigators find one feature in common; that in all cases where columnar growth was observed the metal that was diffusing into iron had the property of preventing the formation of the gamma solid solution when a definite percentage of the alloying element was reached. Furthermore, these authors found that if the diffusion experiments were conducted at temperature below the so-called "gamma loop" range of

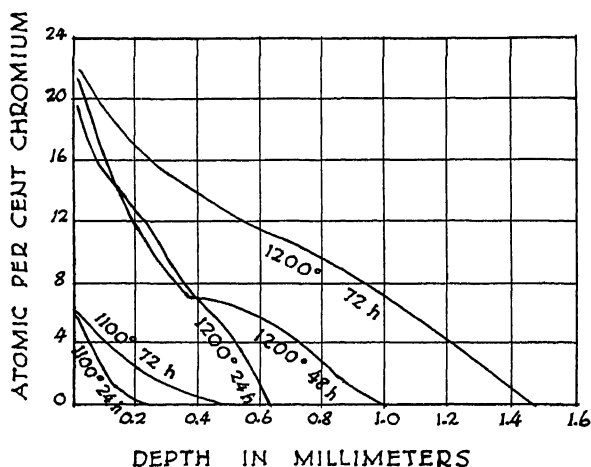


FIG. 1.—DEPTH-CONCENTRATION CURVES OBTAINED BY GRÜBE AND FLEISCHBEIN.

the iron-tin system, no columnar growth appeared and the diffusion line was absent. The theories of Grube and Kelley cannot account for this phenomenon in a satisfactory manner. Thus, Bannister and Jones propose the following mechanism for the process: That diffusion above the Ac_3 transformation, up to the necessary extent to inhibit the gamma phase, proceeds without any re-orientation of lattice; that subsequent diffusion causes the production of a new solid phase (alpha solid solution), the nuclei of the new phase being immediately absorbed by the growing crystals.

EXPERIMENTAL WORK

In the present paper use is made of sides of the unit body-centered cell of iron-chromium alloys obtained by G. D. Preston. This work is

⁴ C. O. Bannister and W. D. Jones: The Diffusion of Tin Into Iron. *Jnl. Iron and Steel Inst.* (1931) **124**, 71.

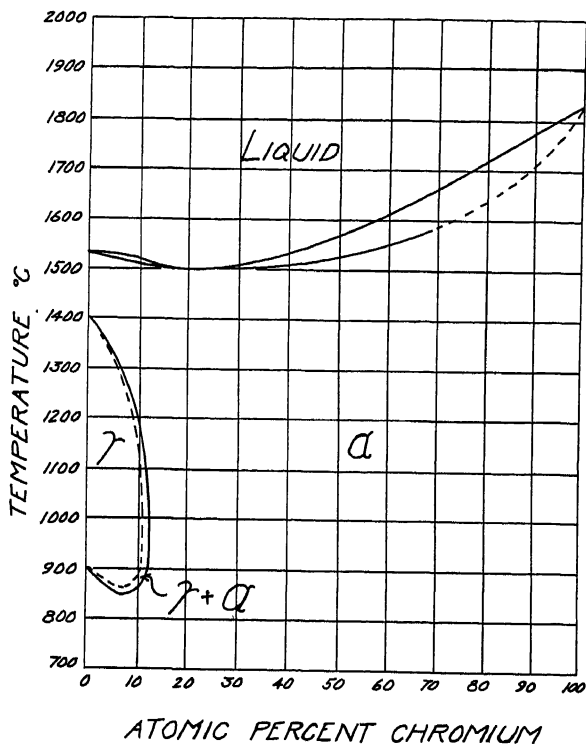


FIG. 2.—IRON-CHROMIUM CONSTITUTIONAL DIAGRAM ACCORDING TO ADCOCK.

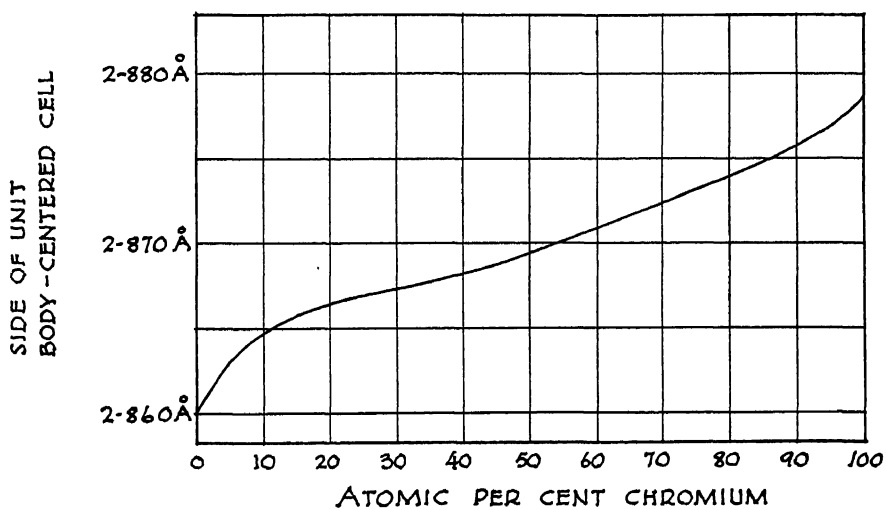


FIG. 3.—SIZE OF UNIT CELL OF IRON-CHROMIUM ALLOYS ACCORDING TO PRESTON.

given as a supplement to a paper by Adcock⁵ on the iron-chromium constitutional diagram. The diagram obtained by Adcock is given in Fig. 2, the magnetic transformations being omitted.* Fig. 3 reproduces Preston's plot of cell size against percentages of chromium in the alloys.⁶ The values are said to be accurate to 0.0005\AA .

The specimen used consisted of a piece of electrolytic iron approximately 5 by 1 by $\frac{3}{8}$ in. packed in powdered electrolytic chromium in a spinel crucible. The chromium was powdered in an iron mortar to pass a 100-mesh screen. The specimen was treated in a vacuum furnace designed and constructed for this purpose. The furnace consisted essentially of a platinum-wound resistance unit mounted inside a glass bell jar. The base of the furnace was a ground-glass plate cemented to a steel plate. Temperature measurement and control was obtained by use of a calibrated platinum, platinum-rhodium thermocouple. The auxiliary equipment consisted of a standard calibrated vacuum gage, a mercury vapor pump backed by a mechanical pump, and a controlling pyrometer. By means of this apparatus specimens were heated for 96 hr. at 1200°C . under an average pressure of 0.020 mm. of mercury.

Because of the relatively small difference between the side of the unit body-centered cell of iron and that of chromium, it was necessary to use a method of X-ray measurement capable of considerable precision. Dr. Charles S. Barrett, of the Metals Research Laboratory, Carnegie Institute of Technology, kindly submitted a photograph of a Sachs type camera used by him, in accordance with which a camera of somewhat similar design was constructed.

The source of radiation was a Shearer type, self-rectifying tube operated at 10 ma. and 35 kv. An exposure of 2 hr. was found sufficient. The radiation was that of the K-alpha doublet of chromium.

When the specimen was examined after treatment, it was found that the powdered chromium had sintered, giving a coherent mass which could be broken from the metal in large pieces. The surface of the metal thus exposed was very brilliant and even. The only evidence of oxidation was a green coloration at the outside surface of the sintered material. The specimen was sectioned, polished, etched, and examined microscopically.

For the X-ray investigation, a small section of the original specimen was ground to successive depths on a plane perpendicular to the direction of diffusion. The grinding was done by hand on No. 1 polishing paper, finishing on No. 00 paper. The depths were checked by means of an ordinary outside micrometer. No effort other than ordinary care was made to keep the ground surface parallel to the original surface, since

* See author's discussion, page 177.

⁵ F. Adcock: The Iron-Chromium Constitutional Diagram. *Jnl. Iron and Steel Inst.* (1931) **124**, 99.

⁶ Also published by G. D. Preston independently: An X-Ray Examination of Iron-Chromium Alloys. *Phil. Mag.* (1932) **13**, 419.

measurements with the micrometer were made at the same place each time, and since the X-ray beam had a diameter of not more than $\frac{1}{16}$ in. and was centered in the mark left by the micrometer anvil.

A portion of the sintered material broken from the surface of the specimen was also subjected to X-ray examination. The material was sufficiently coherent to be suitable for grinding off thin layers very easily, the depths being measured by a micrometer as before.

RESULTS OBTAINED AND CONCLUSIONS REACHED

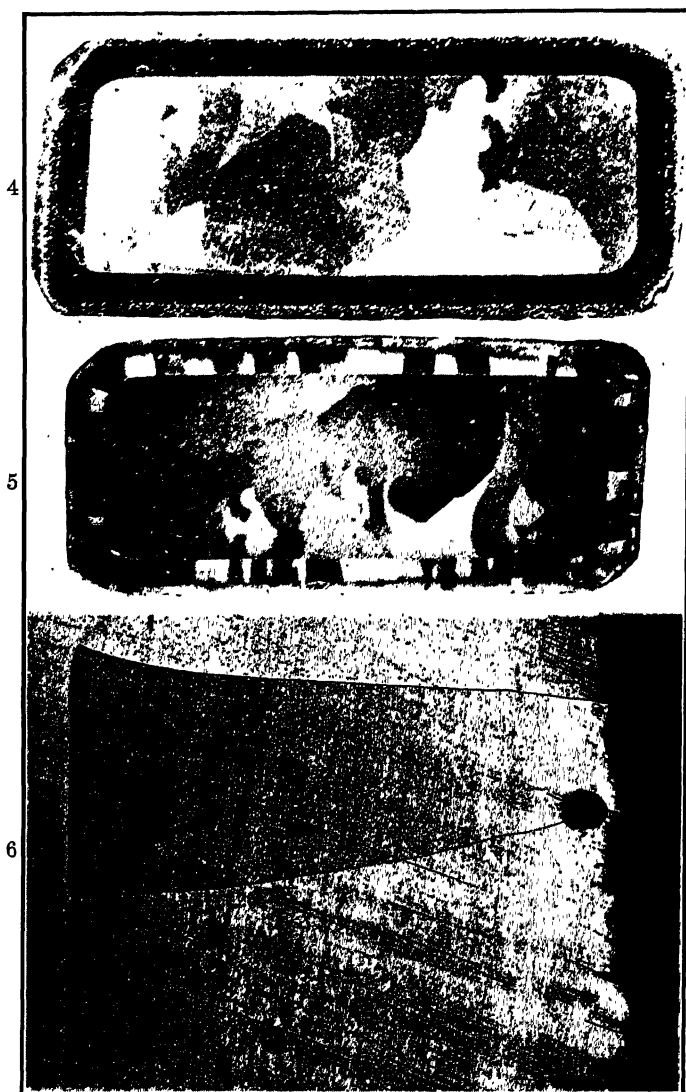
The metallographic examination of the specimen after diffusion had taken place showed little that has not been observed by previous investigators. A few points, however, should be mentioned. Fig. 4 shows a cross-section of the specimen at a magnification of five diameters, etched with nital. It will be noted that the line of demarcation between the etched and unetched portion of the surface is very sharp and follows the outer contour of the specimen remarkably.

Fig. 5 shows the same cross-section at a slightly lower magnification etched with $\text{FeCl}_3 + \text{HCl}$. Here the columnar nature of the grains in the outer zone is clearly evident. Fig. 6 is a portion of the same specimen at a magnification of 100 diameters and shows the surprisingly straight boundary between the two zones. Close examination will reveal the polishing ridge just inside the boundary line. This ridge is quite evident to the unaided eye even after rough grinding of the surface and would seem to indicate a sharp change in the hardness of the specimen. It is rather difficult to reconcile so abrupt a change in the hardness with a gradual concentration gradient as shown by the diffusion curves of Grube given in Fig. 1.

In Fig. 6, when the boundary line between the two zones crosses a grain boundary between the columnar grains, a pronounced V is formed, the apex extending away from the coarse-grained material in the interior. This phenomenon was found consistently and its explanation might be of considerable interest. The boundary line seems to be lacking at the upper left-hand side of Fig. 6, an effect observed and explained by previous investigators.

In order to coordinate the measurements of the side of unit cell at various depths through the diffusion zone with the percentage of chromium present, the data of Preston previously referred to are used with a slight modification. The lattice parameter of the chromium used in this investigation checked exactly with that used by Preston (2.8786\AA), but in the case of the electrolytic iron there was some difference. The value obtained in the present instance was 2.8608\AA while that of Preston was given as 2.8600\AA . The correction factor was introduced in the following manner; Preston's values were carefully plotted for the entire range from 100 per cent iron to 100 per cent chromium. A second curve was then

plotted with a difference of 0.0008\AA . at 100 per cent iron and a difference of 0.0000\AA . at 100 per cent chromium, the intermediate differences being proportional to the concentration. From the corrected curve, values



FIGS. 4-6.—CROSS-SECTION OF IRON-CHROMIUM SPECIMEN AFTER DIFFUSION HAD TAKEN PLACE.

FIG. 4.—Etched with nital. $\times 5$.

FIG. 5.—Etched with $\text{FeCl}_3 + \text{HCl}$. $\times 5$.

FIG. 6.—Etched with $\text{FeCl}_3 + \text{HCl}$. $\times 100$.

for the percentage concentration were obtained from the parameters measured at intervals through the diffusion zone. See Fig. 7.

A consideration of the diffusion curve thus obtained leads to an immediate explanation of the etching and polishing effects observed. The concentration falls off gradually for a considerable distance, then drops very abruptly, finally reaching a point where no chromium is present. This drop in concentration is so abrupt that when the specimen has been ground to the point where etching with nital discolors a portion of the surface (indicating that the boundary has been broken through) a spectrogram of the unetched area indicates 15 per cent chromium, the lines being sharp and distinct, while a spectrogram of the etched area indicates

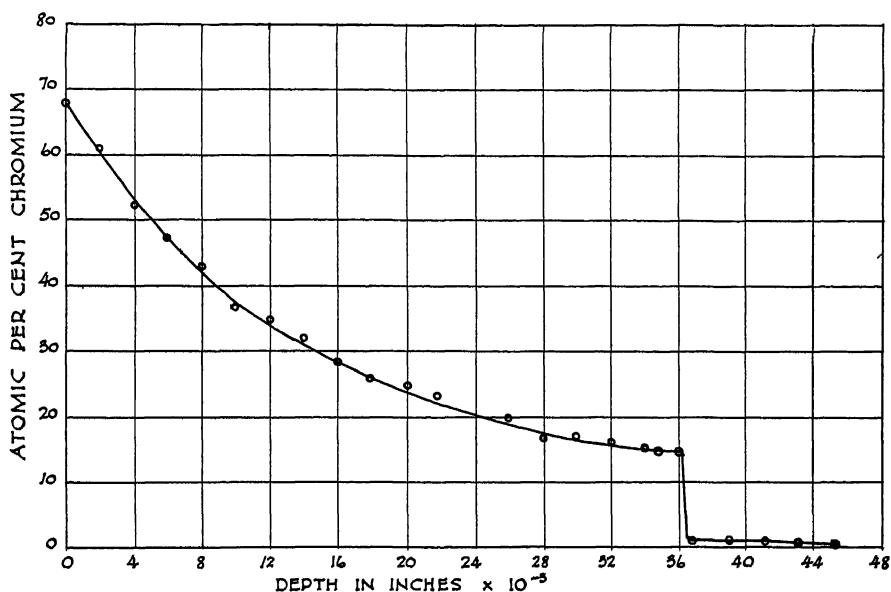


FIG. 7.—DEPTH-CONCENTRATION CURVE.

less than one per cent chromium. Moreover, with the specimen placed on the X-ray camera in such a position that the beam strikes a portion of both areas, a film was obtained showing two distinct pairs of the K-alpha doublets, one pair for each concentration.

Table 1 gives all X-ray data. In the data on the sintered material broken from the surface of the specimen, it will be noted that there has been a very considerable penetration of iron into the chromium powder.

For the most part, the lines on the spectrograms were distinct and sharp, permitting very accurate measurement. In three cases, however, in the region of high chromium content, films were obtained showing two distinct pairs of doublets. This was thought to be due to the fact that the X-ray beam struck grains of slightly different concentrations. If, in these cases, the lines were averaged in their measurement, the points were found to fall well on the curve.

As for the accuracy of the methods, it is believed that the lattice parameters are correct to 0.0003\AA ., and this, assuming Preston's values and the deviation curve to be correct, will give an accuracy of ± 1 atomic per cent concentration in the high-iron region, and ± 3 atomic per cent in the high-chromium region.

The percentage of chromium at the break in the curve is somewhat greater than that indicated by Adcock's diagram as the limit of the gamma solid solution range at 1200°C . Owing to the difficulty of determining these points on the equilibrium diagram, it may be that the gamma solid solution limit at 1200°C . is somewhat greater than that indicated by Adcock's diagram. Others⁷ have placed the limit at 14 or 15 atomic per cent chromium, figures more in agreement with the present results.

When this work was started, it was hoped that the coincidence between the limit of the gamma loop at the diffusion temperature and the chromium content at the boundary line could be proved by the presence of lines from the gamma structure on the X-ray spectrograms of specimens quenched from the diffusion temperature. Reference to the diffusion curve obtained will show that this would be impossible because the drop in concentration is so abrupt that the quantity of material that would be retained in the gamma form would be insufficient to give a diffraction pattern. This was found to be the case. However, a specimen previously treated for diffusion at 1200°C . was water-quenched from 1350°C . and, in this case, the boundary line occurred at 8 per cent chromium instead of 15 per cent, a result that obviously is due to the narrowing of the gamma solid solution range at higher temperatures.

From these results it may be concluded that the mechanism of the diffusion process is exactly as set forth by Bannister and Jones. The shape of the diffusion curve is not as found by previous investigators. Instead of merely a change in slope at the position of the boundary, there is an abrupt drop in concentration. The apparent discrepancy in these results is easily accounted for. Previous experimenters have obtained their depth-concentration values by the chemical analysis of lathe turnings from cylindrical specimens. Thus, so abrupt a drop in concentration would necessarily be obscured by the thickness of the layer that must be turned off for analysis.

Previous investigators have assigned the change of slope in the diffusion curve to the fact that it will be more difficult for atoms to migrate across the region of disorganization between the two phases

⁷ E. C. Bain: The Nature of the Alloys of Iron and Chromium. *Trans. Amer. Soc. Steel Treat.* (1928) 9, 9.

P. Oberhoffer and C. Kreutzer: Beiträge zu den Systemen Eisen-Silizium, Eisen-Chrom, und Eisen-Phosphor. *Stahl und Eisen* (1929) 49, 189.

TABLE 1.—*X-ray Data*

Depth, In.	Side of Unit Cell, Å.	Atomic Per Cent Chromium
0	2.8721	68
0.002	2.8712	61
0.004	2.8700	52
0.006	2.8694	47
0.008	2.8688	43
0.010	2.8684	37
0.012	2.8682	35
0.014	2.8679	32
0.016	2.8677	28
0.018	2.8675	26
0.020	2.8674	25
0.022	2.8673	23
0.024	2.8669	20
0.026	2.8669	20
0.028	2.8667	18
0.030	2.8667	18
0.032	2.8666	17
0.034	2.8663	15
0.035	2.8662	14
0.036	2.8663	15
0.037	2.8614	1
0.038	2.8614	1
0.039	2.8611	0.5-1
0.041	2.8612	0.5-1
0.043	2.8610	0.5
0.045	2.8608	0

	DEPTH, IN.	SIDE OF UNIT CELL, Å	ATOMIC PER CENT CHROMIUM
Specimen water-quenched from 1200° C., ground to border and etched with nital.	Unetched area.....	2.8663	15
	Etched area.....	2.8612	1
Specimen water-quenched from 1350° C., ground to border and etched with nital.	Unetched area.....	2.8652	8
	Etched area.....	2.8610	0.5
Sintered material broken from surface of specimen.	0.....	2.8746	83
	0.004.....	2.8648	85
	0.008.....	2.8758	89
	0.014.....	2.8764	93
	0.018-0.038 films unmeasurable—doublets not resolved ^a		
	0.043.....	2.8786	100

^a The indistinctness of these films is probably due to nonuniformity of composition.

ANALYSIS OF MATERIALS USED, PER CENT

ELECTROLYTIC IRON		ELECTROLYTIC CHROMIUM	
Carbon.....	0.065	Carbon.....	0.043
Phosphorus.....	0.006	Iron.....	0.067
Sulphur.....	0.004	Aluminum.....	0.042
Silicon.....	0.006		

existing at the temperature of diffusion. From the results given in this paper, it would seem that this explanation is not entirely satisfactory.

The slope of the diffusion curve as presented in this paper offers an explanation of the polishing and etching effects in that there must necessarily be an abrupt change in hardness and resistance to chemical attack, corresponding to the abrupt change in concentration in the specimen.

ACKNOWLEDGMENT

The author wishes to acknowledge the cooperation of Prof. Robert S. Williams, Prof. John T. Norton and associates in the Department of Metallurgy, Massachusetts Institute of Technology; also the assistance of Dr. Charles S. Barrett of the Metals Research Laboratory, Carnegie Institute of Technology.

DISCUSSION

(John Johnston presiding)

J. JOHNSTON,* Kearny, N. J.—Diffusion in metals is a topic upon which our general ideas are still far from satisfactory; and they can become satisfactory only by work, such as has just been presented to us, which brings us thoroughly reliable information.

V. N. KRIVOBOK,† Pittsburgh, Pa.—The contribution on the subject of diffusion in solids should be of much interest to us, not only because of its broad theoretical aspects, but also because of its importance in productive, creative work. A search of the literature pertaining to the question of diffusion in solids produces numerous references, but very few contain the results of completed investigations in the field of ferrous alloys.

My remarks pertaining to the paper are not uttered in the spirit of criticism but merely as suggestions for the author's consideration. In my opinion extraordinary care should be exercised in selecting the materials for diffusion work. Dr. Hicks mentions that the specimen used for experimental work consisted of a piece of electrolytic iron. Since we know that the composition of electrolytic "iron" may vary considerably, it is important to know exactly the impurities present in the iron. Diffusion phenomena and solid solubility, of course, are, intimately related and the factors influencing one should also influence the other. I have suspected for some time, and my views were upheld last night during a discussion with one of my friends, that the existing data on the solubility of carbon in chromium alloys is in need of correction. Even small amounts of impurities influence the solubility. These impurities are not limited to carbon, silicon, manganese, nickel, etc. Others, less commonly thought of in connection with metals, are known to exert considerable influence on the general phenomenon of phase changes, as reflected by definite modifications in certain properties. It is to be anticipated that some impurities—nitrogen, for example—may, in some way, influence the rate of diffusion, therefore it is desirable to work with the purest obtainable materials, when the aim of the research work is of such general interest as the present investigation. These remarks, may I repeat, are not designed to minimize the value of the paper. I have always believed in a preliminary survey of the field before undertaking more refined work.

* Director of Research, U. S. Steel Corporation.

† Associate Professor of Metallurgy, Carnegie Institute of Technology.

The sharp break as shown in the curve for depth versus concentration is very disconcerting. Granting that the diffusion rates in alpha and gamma iron are widely different, the shape of the curve as given does not show the existence of heterogeneous (alpha plus gamma) field. Had the method that Dr. Hicks employed been less sensitive, it would not have been so difficult to find the explanation. As it stands, the explanation is by no means simple and I believe that Dr. Hicks himself would want to pursue the subject still further, as I hope he will.

W. P. DAVEY,* State College, Pa.—There are, in general, only two types of theories possible as to the nature of a solid solution. We have been studying for some time as to what we mean by solid solution and we believe that there is some evidence that there is a tendency toward a chemical combination between solubility and solvent. We do not want to press that too far at this time, but it does leave us with two alternatives, either the soluble material can travel along by diffusion, atom by atom, each atom being entirely independent of every other atom then, or it can tend to aggregate in little clusters, in which case diffusion could only go on by the breaking up of individual clusters. If Dr. Hicks could confirm his present data by having a large number of curves in a large number of specimens of pure material, so that we could be really sure of that straight drop from 15 per cent to 1 per cent, we might be able to say that one of those two alternatives was wrong. Not that the other one was right, but at least we could say that one was wrong. If the drop off is not there, it would be reasonable to assume that diffusion occurs atom by atom, the atoms just migrate along, as we have ordinarily pictured them. If instead of that, the drop off is really there, it would look as though the chromium were in little aggregates of some loose kind of chemical combination between the chromium and the iron, and that the aggregates, call them colloidal aggregates if you will, would have to disintegrate in order that diffusion might occur. In such a case one would expect a much sharper boundary line between the chromium-containing material and the pure iron into which diffusion was occurring.

I hope that Dr. Hicks can manage to get still purer materials and do a very large number of measurements of this sort, in the hope that he can decide between these two alternatives.

J. T. NORTON,† Cambridge, Mass.—It is true that sometimes we cannot be certain of the interpretation of the X-ray evidence, but here a measurement of a lattice parameter is unquestionably an indication of chemical composition, and this work illustrates in an excellent manner that the X-ray results are definite and reproducible. The points shown by Dr. Hicks lie closely on a smooth curve and they could be duplicated time and time again. I think the results show very plainly the definite progress that has taken place during the last few years and indicate that the precision claimed for the method is, in this case at least, really justified.

J. JOHNSTON.—It would be very desirable if measurements of diffusion rate, such as those of Dr. Hicks, were extended to a series of temperatures; because from the temperature coefficient of the rate one could calculate the corresponding heat effect and compare it with, for instance, the heat of solution measured in other ways. This should aid us in interpreting the data, in ascertaining in how far the several data are consistent; and if they are not, an analysis of the data would lead to a reinvestigation of the more doubtful and thereby bring about a greater degree of certainty in our knowledge of the matter. I find difficulty in making a useful picture of the

* Professor of Physical Chemistry, Pennsylvania State College.

† Associate Professor of Metallurgy, Massachusetts Institute of Technology.

process of diffusion through a metal, except possibly in the case of hydrogen, which is so small and so neutral chemically to metal atoms that it can be regarded as passing through the lattice structure without affecting it appreciably. There is one indication, however, which seems inherently probable and worth following up; namely, that, other conditions being equal, diffusion is slower the greater the chemical attraction between the diffusing atom and the metal atom; for instance, the rate of diffusion through iron of oxygen is very much smaller than that of carbon at the same temperature, a much greater difference than could be attributed merely to the different atomic size of the two substances. We need reliable information covering a wider range of conditions and a larger number of pairs of diffusing substances, and secured by as many independent methods as are possible. It is to be hoped that a more widespread recognition of the fundamental importance of diffusion through metals will lead to further experimental work along these lines.

L. C. HICKS.—The discussion has brought to mind several points which should, perhaps, have been brought out in the original presentation. Several have brought up the question of purity of materials. I fully appreciate that impurities may have considerable effect on phenomena of this type, but I believe that in this case the phenomenon itself is so gross as to justify the conclusions. Furthermore, the fact that the sizes of the unit cells of iron and chromium checked those of the carefully prepared materials of Mr. Preston was taken as an indication that these materials would be suitable for the method used.

Dr. Johnston has suggested that several other temperatures should have been employed. In order to investigate the effect of other temperature, the following additional experiment was carried out. A specimen that previously had been treated for diffusion at 1200° C. was heated to 1350° C. and quenched in water. This specimen was then subjected to X-ray measurements as before, but in this case the abrupt drop in concentration occurred not at 15 atomic per cent but at 8 atomic per cent, corresponding to the narrowing of the gamma field at the higher temperatures. This was taken as proof of the direct dependence of the concentration phenomenon upon the phase change in the system. This result is further substantiated by the work of Bannister and Jones on the iron-tin system, these investigators having found that when diffusion took place at temperatures above or below the gamma loop range, no columnar growth resulted and the diffusion line was absent.

It has been suggested that it would be of value to extend the time of the diffusion experiment. Unfortunately, the time for the research itself was rather limited. It is believed, moreover, that the results of Grube and others indicate clearly that extending the time of diffusion will have the effect of extending and flattening the diffusion curve, although the general contour will remain the same.

W. B. ARNESS,* Baltimore, Md.—Dr. Krivobok made the point that a sharp drop in chromium content at the inner edge of the diffusion zone is unexpected and in connection with this I wish to mention that the photographs shown in the paper are most interesting, and would in my experience bear out the author's contention that a sudden change in chromium concentration has taken place. The structure of the skin is typical of a high-chromium alloy almost completely decarbonized. The grains themselves are similar in size and orientation to surface grains of decarbonized iron-chromium alloys.

W. D. JONES,† London, England (written discussion).—It is very gratifying to find the "gamma-loop" diffusion theory for chromium and iron so clearly demon-

* Melting Superintendent, Rustless Iron Corporation.

[† The Sir John Cass Technical Institute.

strated. Mr. Hicks is to be congratulated on the close agreement between his results and the investigation of F. Adcock.

The sharp concentration drop from 15 to 1 per cent of chromium reveals how considerable is the force necessary to cause diffusion in a gamma lattice and reorientation to an alpha lattice. The V-shaped groove where the diffusion line meets a boundary originates possibly in the obstruction caused by irregular atomic orientation at the boundary.

It is interesting that chromium first depresses the A_3 point before finally elevating it. Working just below 900°C ., it should be possible to obtain *two* diffusion lines. This effect is apparently seen in Fig. 8, showing diffusion after 8 hr. at 875°C . The limit of penetration of chromium is indicated by the depth of etching.

Concerning minor details, it might be asked why Dr. Hicks did not work at 1150°C ., midway between 900° and 1400° , or alternatively, at about 1000°

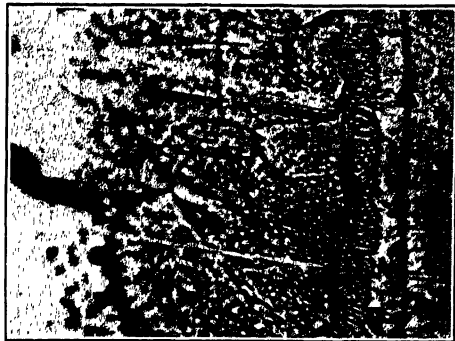


FIG. 8.—DOUBLE DIFFUSION LINE. $\times 1000$.

C ., which appears to be the temperature of the gamma limit. It is also suggested that possibly more regular diffusion might have been obtained by employing powder of at least 200 mesh tightly compressed around the specimen.

F. C. KELLEY,* Schenectady, N. Y. (written discussion).—The X-ray investigation described in this paper has been conducted in a very orderly and exact manner, and can leave no doubt as to the concentrations of chromium on either side of the boundary line between the grains of high and low chromium content.

There has been much added to the literature since the presentation of my paper in 1928.⁸ The fundamental knowledge concerning the influence of Co, Mo, W, Si, Sn, etc. upon the extent of the gamma range was taken into consideration in the preparation of my paper, the purpose being to create more interest and extend the field of knowledge by encouraging the use of X-ray methods in the investigation of this most interesting subject.

The hypothesis put forth was to give a new point of view and to call attention to another factor that seemed of great importance; namely, the force of diffusion.

The discussion of my paper by Zay Jeffries, C. Benedicks and A. Hultgren brought out the importance of the influence of the gamma-alpha transformation upon the progressive growth of the alpha phase caused by the diffusion of various elements.

In that paper I expressed the idea that "The surface grains of iron absorb the particles of powdered material, and the direction of diffusion of the material determines the direction and position of the long axes of the grains." This was really the fundamental idea that prompted the writing of the paper.

Bannister and Jones gave a very able discussion of this diffusion phenomenon along the same lines as Jeffries, Benedicks and Hultgren when commenting on my paper, but said, "The actual orientation of the columnar crystals can only be determined with certainty by X-ray measurements, which have not yet been carried out, but there is some ground for supposing that a certain preferred orientation would be found to be possessed in common by the entire band of crystals. Since, with the

* Research Laboratory, General Electric Co.

⁸ Reference of footnote 3.

progress of diffusion, an entirely new lattice is being produced, it is reasonable to suppose that the orientation of the new lattice would be related in a definite manner to the direction of diffusion, and such a relationship has been demonstrated in the case of the diffusion of zinc in copper by Constance F. Elam."

It may yet be demonstrated, to quote from my paper, that "the reason for sharp falling off in the rate of diffusion at a penetration corresponding to the dark line might be accounted for by the consumption of an enormous amount of energy required to transfer an atom through the distorted area from one orientation to another." I referred to the orientation of the grains with respect to the axis of diffusion. If grains on either side of the dark line can be analyzed for the percentage of chromium, a like analysis of those grains extending across this region but exhibiting no sharp dark line might reveal a different concentration of chromium on the low-chromium side of the invisible line, when compared with those exhibiting the dark line. This would give an indication of the influence of this so-called distorted region on the rate of diffusion.

If the orientations of these grains could be established on either side of the dark line and the invisible line with respect to their long axes, the influence of orientation upon rates of diffusion might be established.

F. ADCOCK,* Teddington, Middlesex, England (written discussion).—Fig. 2 of the author's paper did not strictly represent the writer's diagram. The writer did not determine the inner lines of the "gamma" loop and consequently his diagram did not show them. When investigating this region of the diagram he noticed, however, that thermal and dilatometric changes denoting the limits of the loop usually occurred at higher temperatures when observed on a rising temperature than did the corresponding reverse changes which were associated with a falling temperature. These two sets of observations were linked by lines in his Fig. 7^o which showed the "gamma" loop in detail, but as these lines did not represent changes occurring under equilibrium conditions they did not find a place in the constitutional diagram (Fig. 8). There, the limits of the gamma loop were shown by a single line obtained from averaged values. He therefore asked that the author in his Fig. 2 should either show the "gamma" loop as a single line or indicate clearly on the same page that the diagram has been modified by the author.

Mr. Hicks is to be congratulated on his novel method, which demonstrated the step in composition connected with the "alpha-gamma" change. It should be noted, however, that the iron used by him contained 0.065 per cent carbon, the chromium 0.043 per cent carbon and that no analysis for oxygen in the chromium was given.

Electrochromium as deposited may contain oxygen equivalent to more than 1.5 per cent of chromic oxide. The limits of the "gamma" loop are apparently influenced by the presence of relatively small amounts of impurities and for this reason it would be of great interest if the author could repeat his experiment using purer materials.

G. D. PRESTON,† Teddington, Middlesex, England (written discussion).—I would like to suggest that in discovering an abrupt break in the composition-depth curve where it falls from 15 to 1 atomic per cent chromium, Dr. Hicks has in fact determined the solubility limit of chromium in γ iron as well as the composition of the α phase in equilibrium with it at 1200° C. It may be objected to this interpretation of the observed effect that the system is not in equilibrium. But I suggest that as the rate of diffusion is small and that as the concentration gradient at both sides of the discontinuity is also small, equilibrium conditions are *approximately* obtained at the

* National Physical Laboratory.

^o Reference of footnote 5.

† National Physical Laboratory.

boundary of the two phases. This last consideration is the more important and Table 1 shows that in the range of depth from 34 to 36 thousandths of an inch there is no detectable change of composition; i.e., the gradient is less than 1 atomic per cent chromium in this interval of 2×10^{-3} in. Dr. Hicks attributes his failure to detect the presence of the γ phase to the minute quantity present, but it is possible that the phase has not been preserved by the quench and that it has reverted to the α state.

The difference between Dr. Hicks' figure of 15 atomic per cent chromium for the limit of the γ loop and the diagram of Fig. 2 may be due to differences in purity of the materials as suggested by Dr. Adcock above or to the fact that equilibrium conditions are only approximately attained. It would be interesting to know if Dr. Hicks has examined any specimens in which the chromium has been allowed to penetrate to greater depths and, if so, whether the discontinuity always occurs at the same composition. One would expect failure to obtain equilibrium to give too high a chromium content for the α phase and too low a figure for the transformed γ phase.

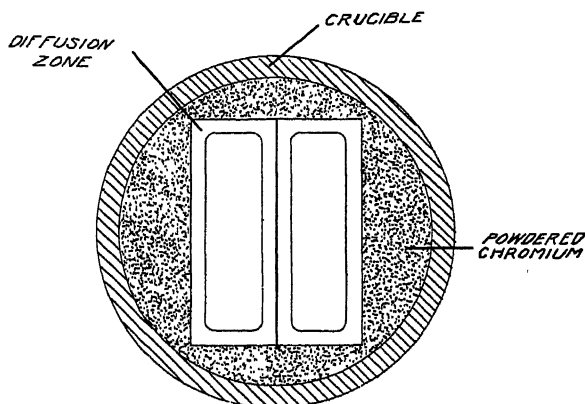


FIG. 9.

The discrepancy between Dr. Hicks' figure for the parameter of electrolytic iron and the value given by me for the high-purity iron used by Dr. Adcock may have some significance, although the difference amounts only to the sum of our errors of observation. I believe the parameter of electrolytic iron is slightly larger than that of the same material remelted in vacuo but would be glad to know if Dr. Hicks can confirm this from his own experience.

L. C. HICKS (written discussion).—I feel that I owe Dr. Adcock a profound apology for the manner in which I have reproduced his diagram. Due to an oversight I failed to include a notation to the effect that Dr. Adcock's diagram had been modified to the extent of showing the gamma loop as a conjugate line. I have submitted a corrected diagram for the final publication of this paper. I am extremely interested in the suggestion by Mr. Preston that my results may be interpreted as a determination of the solubility limit of chromium in gamma iron as well as the composition of the alpha phase in equilibrium with it. I hope that at some time I may be able to extend this work so as to verify this interpretation, which I believe to be correct. Mr. Preston has inquired about the variation of the parameter of electrolytic iron with the melting conditions. I understand that Prof. John T. Norton, at the Massachusetts Institute of Technology, has confirmed the result suggested by Mr. Preston, in that it was found that electrolytic iron had a slightly different parameter depending upon whether it was annealed as deposited, remelted in vacuo, or treated in hydrogen.

I believe that Dr. Jones' suggestion concerning the V-shaped groove gives a reasonable interpretation of the phenomenon. The fact that this condition is always observed at the boundary between adjacent columnar grains would indicate that the effect is related to the disorganized condition of the lattice that would be expected at this point. I am very pleased that Dr. Jones has submitted the photomicrograph showing the double diffusion line. The actual demonstration of a phenomenon that could be predicted from other results lends considerable support to the proposed theories. I hope that at some time I shall have an opportunity to subject a specimen such as Dr. Jones pictures to an X-ray study of the concentration changes. Such an experiment should reveal two distinct breaks in the depth-concentration curve.

Dr. Jones has suggested the use of a more finely ground powder tightly compressed around the specimen, in order to produce a more regular diffusion. Several preliminary experiments were conducted in order to determine the effect of the contact between the specimen and powder. Three types of specimens were employed, one electroplated with chromium and then packed in powdered material, one sprayed with chromium and packed, and one simply packed in powdered chromium. These were heated in vacuo under identical conditions and the microstructures indicated no difference, either in depth or regularity of the diffusion zone. After this work was completed a further experiment was conducted giving results which I believe to be most interesting. Two pieces of electrolytic iron measuring approximately 3 by 1 by $\frac{1}{4}$ in. were placed side by side and packed in powdered chromium as shown in Fig. 9. There was no powdered chromium between the specimens. The materials were then heated in vacuo for 96 hr. at 1200° C. After treatment the pieces were cross-sectioned, polished and etched. The results were rather surprising in that the penetration of chromium was absolutely even on all sides of the specimen, although only three sides were actually in contact with the powdered material. Since all materials are solid at the temperature of the diffusion process, the results would seem to indicate that there is some appreciable vapor phase of chromium present to cause the penetration at the inner surfaces.

At the beginning of this research it was hoped to carry out an X-ray investigation of the orientation of the columnar grains. Unfortunately, owing to the difficulty involved and the lack of time and facilities, it could not be undertaken. I fully agree with Mr. Kelley that such work would be of great value in clearing up the question and I have little doubt that the results will show that the orientation of the columnar grains bears a definite relationship to the diffusion direction, providing, however, that the progress of diffusion involves a phase change such as exhibited by the iron-tin and iron-chromium systems, since it was found by Bannister and Jones that no columnar growth resulted if the diffusion temperature was outside the gamma-loop range.

Diffusions that Take Place in Iron-silicon Alloys during Heat Treatment

BY N. A. ZIEGLER,* EAST PITTSBURGH, PA.

(New York Meeting, February, 1934)

CONSIDERABLE work has been and is being done on the changes of physical properties that take place in alloys at elevated temperatures, and much information on this subject is published. Much less is known, as pointed out by Rickett and Wood,¹ about reactions between the alloys and atmospheric gases and still less is known about changes within the alloy itself under the influence of heat and given atmosphere. Moreover, most of the work published has been done on the alloys of "heat-resisting" type, in which chromium is an essential ingredient, the behavior of all other alloys being quite unknown, except perhaps of decarburization produced at the surface by oxidizing atmospheres.

It has been shown² that iron, with total amount of foreign ingredients not exceeding 0.01 per cent, if heated in an oxidizing atmosphere at above 900° C., may be saturated with oxygen to 0.1 per cent. It was suspected that something of a similar nature may take place in iron-silicon alloys (transformer material), the mechanism of such processes being either a direct diffusion of oxygen into the alloy, or oxygen combining with silicon to form SiO₂ or more complicated (silicate) inclusions. Another possibility to be considered was that during annealing in oxidizing atmospheres, when scale is being formed, silicon may oxidize preferentially at the surface, thus impoverishing the alloy in silicon. In collaboration with Dr. T. D. Yensen,³ the writer set out to investigate this problem about two years ago in order to settle these questions.

TESTING PROCEDURE

In the first part of the investigation, two pieces of 4 per cent silicon iron, prepared in hydrogen atmospheres and forged to 3/4-in. square bar,

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* Westinghouse Research Laboratories.

¹ R. L. Rickett and W. P. Wood: *Amer. Soc. Steel Treat. Preprint* (1933).

² N. A. Ziegler: *Trans. Amer. Soc. Steel Treat.* (1932) **20**, 73.

³ T. D. Yensen: *Trans. Amer. Inst. Elec. Engrs.* (1924) **43**, 145.

TABLE 1.—Diffusions in Forged Bars of 4 Per Cent Silicon Iron

Sample No.	Treatment	O ₂ , Per Cent.			H ₂ , Per Cent.			Si, Per Cent.			C, Per Cent.			SiO ₂ , Per Cent
		1 Cut	2 Cut	3 Cut	1 Cut	2 Cut	3 Cut	1 Cut	2 Cut	3 Cut	1 Cut	2 Cut	3 Cut	
AX-4.....	Original	0.004	0.008		0.002	0.002		4.00	4.02	4.06	0.0035	0.0037		
AX-4D.....	Original							4.18	4.18		0.0035	0.0027		
AX-4A.....	Air, 1100° C., 10 hr.	0.008	0.011	0.010	0.003	0.005	0.003	3.97	4.13	4.29				
AX-4B.....	Air, 1100° C., 10 hr.	0.008	0.013	0.016	0.003	0.005	0.005	3.91	4.00	4.14				
AX-4B-1.....	O ₂ , 1000° C., 5 hr.							4.16	4.18	4.18	0.0020	0.0027	0.0043	
AX-4C.....	O ₂ , 1000° C., 5 hr.							4.16	4.17	4.19	0.0024	0.0031	0.0039	
AX-4E.....	H ₂ , 1100° C., 4 hr.							4.19	4.26	4.25	0.0028	0.0038	0.0046	
AX-4F.....	H ₂ , 1100° C., 4 hr.							4.20	4.26	4.24	0.0028	0.0036	0.0046	
AX-4G.....	Vacuum, 1100° C., 4 hr.							4.15	4.28	4.22	0.0034	0.0037	0.0034	
AX-4H.....	Vacuum, 1100° C., 4 hr.							4.17	4.24	4.21	0.0036	0.0037	0.0037	
Scale from AX-4 (A and B) ..	Air, 1100° C., 10 hr.								1.35					1.72
Scale from AX-4 (B-1 and C)	O ₂ , 1000° C., 5 hr.								0.25					0.74

AX-4A and AX-4B, were kept in air at 1100° C. for 10 hr. (Table 1, Fig. 1). After the heat treatment, scale was removed from the surface of the sample and analyzed separately. From all six surfaces of each sample, plates $\frac{1}{16}$ in. thick were machined off and called "first cut." Then a "second cut" and a "third cut" were prepared in a similar way. By analyzing each "cut" separately, the difference in chemical composition could be determined from the surface to the center of the heat-treated

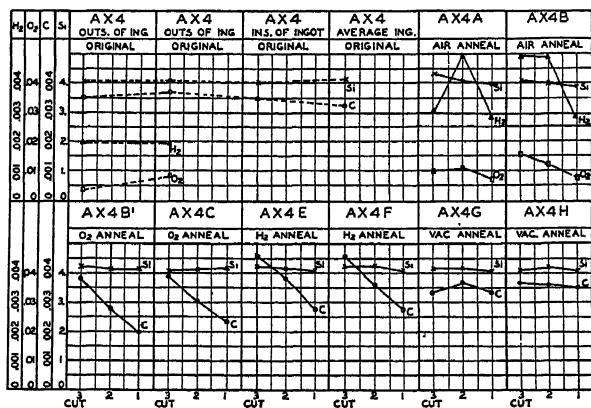


FIG. 1.—DIFFUSION CURVES, FORGED BARS OF 4 PER CENT SILICON IRON.

sample. The homogeneity of the chemical composition of the original bar (before the heat treatment) was determined by taking chemical analysis in several different places. As indicated by Table 1 and Fig. 1, the variation in the chemical composition of the heat-treated samples is within experimental error.

Attention was concentrated on the behavior of silicon and carbon in silicon iron during annealing in different atmospheres. For this reason a set of samples (AX-4B-1, AX-4C, AX-4E, AX-4F, AX-4G, AX-4H, similar to the first two) were prepared from the same material and annealed in different atmospheres (Table 1 and Fig. 1). After the heat treatment, scale was removed from each sample (whenever it was formed) and analyzed separately, and each sample was split into "cuts" and analyzed for silicon and carbon. From Table 1 and Fig. 1 it will be seen that the homogeneity of the silicon content within each sample is not changed by heat treatments. The carbon content, on the other hand, is reduced at the surfaces of the samples by heat treatments in oxygen and hydrogen atmospheres. Vacuum heat treatment does not affect carbon content to any great extent.

Although the results described so far indicated that the chemical composition of silicon iron does not change during heat treatments, this

question was of such great importance that it was decided to repeat the same experiments with as-cast material, not subjected to any previous mechanical or heat treatments. For this reason two 60-lb. melts with 2 and 4 per cent Si were prepared in an induction furnace in hydrogen and solidified in the crucibles. Each ingot thus obtained was machined down to a cylindrical shape and a central hole was drilled through to remove any possible pipe segregations. Each cylindrical shell thus obtained was cut into rings and each ring into segments. (Fig. 2.)

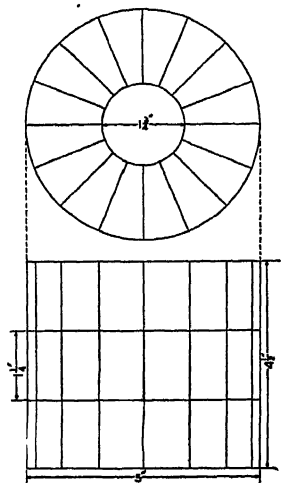


FIG. 2.—MANNER OF CUTTING SAMPLES.

Two segments from the opposite ends of each ingot were machined into "cuts" and analyzed for silicon, carbon and oxygen as before. The analytical results (Table 2, Fig. 3) indicate that the chemical homogeneity of both ingots was quite satisfactory.

Four segments were taken from each ingot and subjected to 24-hr. heat treatments in air, vacuum and hydrogen at 1100° C. and in oxygen at 1000° C. (oxygen at 1100° C. oxidizes the

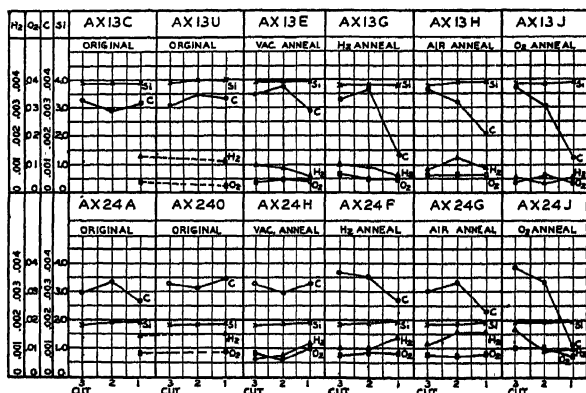


FIG. 3.—DIFFUSION CURVES, SAMPLES OF 2 AND 4 PER CENT SILICON IRON (INGOT MATERIAL).

iron-silicon alloys completely). After removal and analysis of the surface scale, each heat-treated sample was split into "cuts" as before and analyzed for silicon, carbon and oxygen. Results given in Table 2 and Fig. 3 indicate that the chemical homogeneity during the heat treatments is maintained constant, except that carbon is reduced at the surface of samples annealed in hydrogen or oxidizing atmospheres.

Tables 1 and 2 show that generally the scales are lower in silicon than the original material on which they were formed. It was noticed, that,

TABLE 2.—Diffusions in Ingot Material of 2 and 4 Per cent Silicon Iron

Sample No.	Treatment	O ₂ Per Cent			H ₂ Per Cent			Si Per Cent			C Per Cent		
		1 Cut	2 Cut	3 Cut	1 Cut	2 Cut	3 Cut	1 Cut	2 Cut	3 Cut	1 Cut	2 Cut	3 Cut
AX-13C.....	Original	0.004			0.0013			3.88	3.89	3.88	0.0032	0.0029	0.0033
AX-13U.....	Original		0.003			0.0012		3.93	3.94	3.93	0.0038	0.0035	0.0031
AX-13E.....	Vacuum 1100° C., 24 hr.	0.004	0.005	0.004	0.0011	0.0013	0.0010	3.86	3.87	3.86	0.0029	0.0038	0.0035
AX-13G.....	H ₂ , 1100° C., 24 hr.	0.005	0.005	0.004	0.0006	0.0009	0.0010	3.86	3.87	3.86	0.0013	0.0037	0.0033
AX-13H.....	Air, 1100° C., 24 hr.	0.006	0.006	0.006	0.0009	0.0013	0.0008	3.91	3.91	3.86	0.0021	0.0032	0.0038
AX-13J.....	O ₂ , 1000° C., 24 hr.	0.004	0.006	0.005	0.0005	0.0003	0.0003	3.92	3.88	3.87	0.0007	0.0032	0.0037
4 per cent Si													
Scale AX-13J.....	Outer layer												
	Inner layer { metallic nonmetallic												
Scale AX-13H.....													
AX-24A.....	Original	0.009			0.0015			1.88	1.86	1.86	0.0027	0.0033	0.0030
AX-28D.....	Original		0.010			0.0016		1.85	1.85	1.84	0.0035	0.0032	0.0033
AX-24A.....	Vacuum 1100° C., 24 hr.	0.010	0.007	0.008	0.0012	0.0008	0.0007	1.85	1.84	1.81	0.0033	0.0030	0.0033
AX-24F.....	H ₂ , 1100° C., 24 hr.	0.008	0.009	0.008	0.0014	0.0010	0.0010	1.82	1.85	1.83	0.0027	0.0035	0.0037
AX-24G.....	Air, 1100° C., 24 hr.	0.008	0.008	0.008	0.0016	0.0016	0.0011	1.80	1.79	1.80	0.0023	0.0033	0.0030
AX-24J.....	O ₂ , 1000° C., 24 hr.	0.007	0.010	0.010	0.0011	0.0009	0.0016	1.82	1.82	1.82	0.0011	0.0033	0.0038
2 per cent Si													
Scale AX-24J.....													
Scale AX-24G.....													

in all cases, between the outer scale crust and the unoxidized material there is a thin, pinkish-white layer. Usually the amount is so small that analysis of it is quite impossible, and only in scale AX-13J (Table 2), which was oxidized to a greater extent than the rest, was this layer found in quantities sufficient for chemical analysis. It was found to be 21.5 per cent silicon, which is fairly close to the chemical formula FeSiO_3 (FeSiO_3 contains 21.2 per cent). This layer probably acts as a film, protecting the underlying material against further oxidation (or contamination with oxygen).

CONCLUSIONS

Although the results described are in general of a negative character a few interesting conclusions may be deduced from them:

It appears that no appreciable diffusion resulting in a change of chemical composition takes place in silicon iron during heat treatments. On the basis of these results some of the previous observations in regard to oxidation and decarburization during annealing under oxidizing conditions (2 and 3) may be explained. When unalloyed iron is subjected to an oxidizing heat treatment, iron oxide scale is formed on the surface, but there is nothing to prevent oxygen atoms from diffusing into the metal and saturating it, if heated to a sufficiently high temperature. On the other hand, in silicon alloys (with at least 2 per cent silicon) a film of iron silicate will be found on the surface, acting as a barrier to the diffusion of oxygen atoms into the alloy. This film, apparently, does not interfere with the diffusion of carbon atoms (present in the alloy) to the surface, where they react with oxygen to form CO and thus escape from the alloy. In other words, this film, rich in silicon, acts as a one-way barrier; it prevents oxygen from diffusing into the alloy but does not prevent the diffusion of carbon to the surface.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. T. D. Yensen for his interest and encouragement in this work, to Mr. A. A. Frey for preparation of the alloys and to Mr. R. H. Wynne for the chemical analyses.

DISCUSSION

(V. N. Krivobok *presiding*)

W. E. RUDER,* Schenectady, N. Y.—Mr. Ziegler, in his usual careful manner, has done a nice piece of work here, but in one connection our experience has been very different. We have found it possible, under certain limited conditions, to lose as much as 2 per cent of silicon from an iron-silicon alloy of the usual transformer type by hydrogen annealing. When an iron-silicon alloy in the form of thin sheets is

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annealed in close proximity to but not in actual contact with unalloyed iron at temperatures of 1100° to 1200°, about the range used by Mr. Ziegler, and in hydrogen, silicon is very rapidly lost from the silicon-iron alloy.

These conditions, of course, are entirely different from those Mr. Ziegler used in his experiments. This was rather puzzling, since we had previously found a lack of diffusion similar to that Mr. Ziegler speaks of. The explanation may be that silicon hydride is formed, but, being very easily decomposed at that temperature, can travel only a very short distance. As soon as it touches the unalloyed iron it decomposes, for the silicon content of the unalloyed iron increases almost but not quite so much as the silicon alloy loses. It was rather surprising because at that temperature we did not expect silicon hydride to exist, even temporarily. Of course, I do not know that it really does, but that is the only explanation I have for that unusual transfer of silicon. The same thing happens in some other alloys, although we have not followed it up very closely. Aluminum will do the same thing, perhaps a little more easily.

In view of Mr. Ziegler's conclusion that the iron silicate that forms on the surface prohibits the diffusion inward of the oxygen, I wonder what his explanation is for the continued loss of magnetic quality with time when silicon steel is annealed in a hydrogen atmosphere that contains only small quantities of water or oxygen.

The only explanation we can make for this deterioration of quality with time is that the silicon becomes slowly oxidized as oxygen diffuses inward. If that is not the case, I wonder what does cause the steel to become increasingly worse with time of anneal when the temperature is higher than that at which solution of oxygen in iron becomes appreciable; that is, somewhere around 850° C.

P. H. BRACE,* Pittsburgh, Pa.—Not being as well versed in some of these things as Mr. Ziegler, I can only hazard a guess. It is probable that these results may not be measuring the quantities involved with sufficient refinement.

A number of years ago it was believed that carbon was insoluble in steel below a certain elevated temperature. Dr. Yensen found, as he pushed his refinements of carbon determination and elimination further and further, that carbon actually was soluble in very small quantities even at room temperature. When he began to eliminate this solid solution carbon, a number of new and very important facts about the magnetic possibilities of materials were revealed.

It is possible that in this case Mr. Ziegler may have been dealing with a very minute solid solubility of oxygen in the silicon-iron alloy. Considerable refinement may be necessary to detect and quantitatively tie this together with magnetic peculiarities where composition variables are beyond the reach of our present laboratory skill. It is almost axiomatic that everything has some solid solubility in everything else. It may be that in this case the limit is beyond our capabilities of measurement, while still high enough to affect magnetic quality.

The mechanism might be visualized as the diffusion of oxygen into the specimen, oxidizing silicon *in situ*, so to speak, and setting up "stranger molecules" (or what others might term colloidal particles) of SiO₂, interspersed throughout the iron-silicon alloy lattice. The resulting lattice strains then being regarded as responsible for poor magnetic properties. I imagine Dr. Ruder can comment on the plausibility of such a theory better than I.

J. ALEXANDER,† New York, N. Y.—Without commenting upon the paper directly, it may be worth while to mention a certain phenomenon that has been called to our

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† Consulting Chemist and Chemical Engineer.

attention by Professor Bechhold, of Frankfort, in connection with some other material. He found, for instance, that if a block of plaster of paris is immersed in a solution of copper sulfate, the block becomes uniformly colored blue throughout, showing that the copper sulfate is uniformly dispersed in the block. If such a block of plaster of paris is dried out and then broken, tests show that practically all of the copper sulfate has diffused to the periphery. The soluble copper follows the water as it diffuses outward.

I wonder whether anyone present can see an application of this principle in the heat treatment of the alloy of the character mentioned. I am not certain myself just what chemical changes might be responsible for the equivalent of a diffusion of solutes, but it is quite conceivable there would be progressive chemical changes, which would lead certain of the materials toward the surface.

V. N. KRIVONOK,* Pittsburgh, Pa.—It seems to me that a number of things that have happened lately would seem to make it incumbent upon someone to raise a challenge to the analytical chemists. I think we must bring our analytical methods to greater refinement if we are going to get the real answer, and I issue a challenge to the analytical chemists to start this work.

A. SAUVEUR,† Cambridge, Mass.—We are told that the carbon content decreases sharply at different levels from 0.001 to 0.003 per cent. I wonder what that means. If a chemist reported that he found 0.001 and 0.003 per cent carbons, I should consider that a very good check. Perhaps I am not acquainted with the analytical methods by which such minute differences may be detected in such a way that they have real significance.

J. ALEXANDER.—Frequently the end products found when the metal is cool may be quite different from the products that exist when the temperature is elevated. It frequently happens in the course of biological reactions that it is exceedingly difficult to determine analytically what the immediate products are. Anyone who will look up the work that has been done in Cambridge on the behavior of muscle will realize how exceedingly difficult it is to deal with things at different temperatures to determine the sequence of chemical changes by which a certain compound is transformed into other compounds. Possibly the X-ray spectrometer may be useful in determining what compounds exist at elevated temperatures.

N. B. PILLING,‡ Bayonne, N. J.—The brief reference to the analytical methods used refers to some previous paper. I am not familiar enough with that to recognize it by title, but I would like to ask if the method used was one that would reduce SiO_2 at very small concentrations.

P. H. BRACE.—Mr. Pilling has asked whether our method of determining oxygen tends to reduce SiO_2 and report as oxygen the portion that is bound up with silicon as SiO_2 in the alloy. I think it is quite possible, because the carbon reduction and the hydrogen reduction method will both tend to report as oxygen the oxygen bound in silica. The following experiment was tried in our laboratories. We took some thin plates of iron, low-carbon, stacked them up in sandwich fashion with a little pure silica between, heated them to about 1200°C . while passing hydrogen over them. The result was that there was silicon pickup in the steel amounting to several tenths of a per cent in a short time. In other words, hydrogen in the presence of iron will

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† Professor of Metallurgy, Harvard University.

‡ Metallurgist, International Nickel Co.

reduce silica, and fairly readily, so that oxygen reported in this paper probably includes oxygen combined with silicon as silica.

That has a bearing on Mr. Ruder's question and I would like to return one to him. When your silicon sheets are annealed in such a way as to deteriorate their magnetic properties, do you find changes in physical properties, such as intracrystalline brittleness, which would indicate stranger atoms or stranger molecules arranged in some regular way, as by substitution in the alloy lattice?

W. E. RUDER.—Not necessarily. I cannot answer that completely because I do not know all the causes for brittleness in silicon steel. It is true, however, that silicon-steel sheet, improperly annealed, will sometimes be very brittle even though it has as little as 2.5 per cent of silicon. Such conditions I have ascribed to some sort of mechanisms such as you have described, possibly to an oxidation of the silicon in the alloy, and in most cases quite definitely to intracrystalline carbide precipitation.

I can corroborate what you have said about the reduction of silica by hydrogen. I would like to see some careful research work done on that particular problem. I do not think that the reduction is complete, at least from my experience, but I am sure that a considerable amount of silica may be reduced in the presence of iron if the temperature is, say, above approximately 1200° C. I do not believe it happens much below that temperature, but the reduction seems to be quite complete at 1300° C. We have made some experiments, but do not consider them to be sufficiently accurate to be considered quantitative.

There is another question that I would like to ask Mr. Brace. There has been a good deal of talk in the literature from various sources and in various connections recently about the reduction of the carbon in an alloy by means of hydrogen. I believe Cioffi said something about reducing carbon and getting high magnetic results in silicon-iron alloys by using a moist hydrogen atmosphere, and that he found it better than dry hydrogen. While this may be true for unalloyed iron, it is contrary to our experience with silicon iron.

Mr. Ziegler shows here that he reduces carbon considerably by annealing in hydrogen at 1100°. Have you found a temperature below which carbon is practically not reduced by hydrogen? We have never been able to show that carbon in these low-carbon alloys will be reduced appreciably at temperatures below approximately 900° C. As you get to 1100° C., or above, the carbon reduction is comparatively rapid. I wonder if that agrees with your experience.

P. H. BRACE.—I think the experience of our laboratory agrees in general with that of Mr. Ruder's. In most of the work on the preparation of magnetic materials, laboratory work at least, temperatures above 900° have been used, in order to get speed and completeness of carbon removal.

The matter of whether the hydrogen is dry or not—that is, what amount of moisture is required or what amount is permissible—is the thing that is not yet well worked out.

In a paper presented some time ago Dr. Austin described his experiments with high-carbon steels. He found that in moist hydrogen he could get very complete decarburization. In an ordinary 1 per cent carbon steel, he got carbon contents down to the order of 0.02 per cent. With dry hydrogen he got some decarburization at temperatures of 850° at periods of 55 hr. With a few milligrams of water per cubic foot of hydrogen he got less decarburization than he did with very carefully dried hydrogen. We think our experimental technique was sound. It has been tried on plain carbon steel and the 1 per cent chromium carbon steel, each containing about 0.9 carbon, so there is apparently an inversion in the effect of hydrogen on the removal of carbon as the water vapor is increased from a very low value to something of the order of milligrams per cubic foot. We have no explanation for that.

S. L. HOYT,* Milwaukee, Wis.—Running through this paper and the discussion, there has been a line of thought which involves the behavior of an iron containing silicon when exposed to an oxidizing atmosphere, or in general the question of the interpretation of data. In that connection, an experience I had a short time ago may be of interest.

In connection with a study of foreign inclusions, I secured a sample which to the best of my knowledge and belief was free from all foreign inclusions. Very fortunately it turned out to be that way because this was the carburized iron regulus from a vacuum fusion for oxygen determination. At that time Dr. Reeve was working on this problem for us, and as a check on the work that he was doing, we examined some of the carburized iron samples.

First of all I wanted to do a little work on inclusion-free material and naturally I did not want some 4 per cent of carbon in the sample. So I then put it through a hydrogen treatment somewhat the same as already has been described here. The sample was in an alundum boat on silica, and was heated at first to a temperature below the milling point of the cast iron and later on to nearly the melting point of iron for quite a long time.

This time, upon examining the sample, I found that it was no longer free from inclusions, and their identification showed that they were high-silica inclusions or silicates.

To make the matter doubly sure, Dr. Reeve took the treated sample, ran it again through his fractional oxygen determination and reported large amounts of oxygen as SiO_2 .

It seems to me that that has a bearing on some of the discussion we have heard here today, and it raises the question: Is it possible for solid iron to dissolve a material like silica? E. C. Bain, in a recent lecture, published a photograph of a steel sample that contains some silicon which had been heated in an oxidizing atmosphere. This sample showed inclusions of the type I have mentioned. I believe the explanation given was that oxygen diffused in and was precipitated as silica, but that is not exactly compatible with the experiment run in hydrogen of which I have just spoken.

On several other occasions it has appeared that iron actually absorbs solid non-metallic impurities by some such process as I have mentioned. In one case a bar of steel was simply heated in a forging furnace, and this sample of steel was found to have a somewhat peculiar surface. A test showed that parts of it were abnormal, whereas the steel by and large was perfectly normal. A microscopic examination showed that the steel contained both iron oxide inclusions and silica inclusions.

If Mr. Brace has any information on this subject, it seems to me it would be of general interest, even in connection with a paper of this kind, which apparently relates to something quite different.

J. J. B. RUTHERFORD,† Kearny, N. J.—Mr. Ziegler has conducted an oxygen annealing experiment on a 4 per cent silicon alloy, and finds by the consistency of his analysis that apparently there is no diffusion of silicon, yet in the oxide scale of the same material he finds 21 per cent silicon. This would seem to me an indication of diffusion of silicon to that oxide layer of the scale.

P. H. BRACE.—In response to Dr. Hoyt, I might ask this question, and he might answer it immediately. How dry was your hydrogen?

S. L. HOYT.—The hydrogen was not particularly dry; it had water vapor in it.

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† Research Laboratories, U. S. Steel Corporation.

P. H. BRACE.—I would suggest this possibility: That during the early stages of decarburization, the high-carbon iron plus the hydrogen caused reduction of silicon and diffusion of the silicon into the alloy. The subsequent oxidizing anneal allowed oxidation of some of the silicon by moisture in the hydrogen after the carbon had gone. Of course, that again brings up the question of diffusion of silicon.

The last question is a very pertinent one. In the absence of data on the analysis of the outer layers of the scale, it is impossible to say whether or not the silicon in the pinkish layer had accumulated there and represented all the silicon in all the metal that was oxidized, or whether there was some slight diffusion of silicon from the alloy very close to the surface. I think that whatever may be the facts as to the diffusion of silicon, we can say that it is very much less rapid than that of carbon. We can homogenize silicon alloys, which indicates that there is a certain slow diffusibility, but I think that considering the depths to which Mr. Ziegler went with his exploratory sampling and the ratios of the changes in composition due to annealing, he shows clearly that the carbon is far more mobile in iron-silicon alloy than is the silicon, and that within the limits of this experiment and the precision of analyses, the iron-silicon alloy oxidizes in such a way that relatively little preferential oxidation of silicon occurs.

S. L. HOYT.—Were those samples examined microscopically?

N. A. ZIEGLER (written discussion).—Mr. Ruder's observations of diffusion of silicon from silicon iron into pure iron are very interesting, and his own explanations of this phenomenon do not need any further comments. In regard to decreasing magnetic quality of silicon iron with prolonged time of annealing, we find that annealing, even in slightly wet hydrogen, improves the magnetic properties up to certain values beyond which they remain nearly constant. Our experiments also indicate that silicon iron may be considerably improved magnetically by annealing at 1400° C. in hydrogen, but the values of maximum permeability and hysteresis have so far not reached the values attained with unalloyed iron. I regret to say that we do not have accurate data as to the minimum temperature at which hydrogen will reduce carbon in iron and silicon iron, but I believe that below 900° C. the elimination will be very slow.

Mr. Alexander's statement in regard to diffusion of copper sulfate through the plaster of paris is very interesting. I am not familiar with anything similar occurring in metallic alloys.

Replying to Dr. Sauveur's and Mr. Pilling's questions, it may be stated that the "Yensen" method of carbon analysis, accurate to within ± 0.0005 per cent C., was used throughout this investigation. Oxygen was determined by our modified graphite-vacuum-fusion method, which completely reduces all common oxides such as iron oxide, silicon oxide, titanium oxide and aluminum oxide.

Mr. Hoyt's information deserves a great deal of consideration. It is possible that silica inclusions were present in the metal he describes at the beginning and that these were reduced by the carbon, oxygen being removed and silicon remaining dissolved in the iron, but probably segregated. When this metal was heat-treated in a hydrogen atmosphere, the small amount of oxygen may have diffused into the decarburized iron, oxidizing the silicon and precipitating it as oxide inclusions. This suggestion is offered only as a possibility. A great deal of work is required to answer it definitely.

Replying to Mr. Rutherford's remark, it is necessary to be reminded that 21 per cent silicon was found only in the thin nonmetallic layer found in small amounts in the surface of the sample, under the metallic scale. The metallic scale itself was considerably lower in silicon than the sample. Consequently, silicon in the non-metallic layer came, not from the sample, but from the metallic scale.

Magnetic Transformation in Carbon Steels during Quenching*

By I. N. ZAVARINE,† CAMBRIDGE, MASS.

(New York Meeting, February, 1934)

AUSTENITE is often defined as a solid solution of carbon or carbide in a nonmagnetic form of iron. Conversely, magnetic measurements are often used by investigators for the purpose of detecting the degree of austenite decomposition after an iron alloy has been subjected to certain thermal or mechanical treatments. Association of the magnetic state with the gamma-phase decomposition is often extended to the alloys of iron with elements other than carbon. Definition of austenite as a nonmagnetic solid solution cannot be accepted in the light of available information without certain reservations. The relation of magnetic transformations with the gamma-phase decomposition in the complex alloys of iron has never been rigorously proved.

The present investigation deals primarily with the magnetic transformation that occurs in carbon steels during the quenching process. The work was further limited to a study of magnetic transformation in carbon steels quenched at such rates as are necessary to retain the product of austenite decomposition in a martensitic state.

PREVIOUS WORK

Considerable information has accumulated in the literature with respect to the magnetic transformation in alloys of iron, but nearly all of it relates to transformations under the conditions of equilibrium between the phases of the alloy. Earlier studies of Hopkinson,†⁽¹⁾ Curie,⁽²⁾ and Honda⁽³⁾ are well known. Investigations of the magnetic

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‡ For references, see bibliography at end of this paper.

transformation in the alloys of iron during the quenching process have been neglected. The author is not aware of any work dealing with that subject except that of Lewis⁽⁴⁾ who demonstrated that an 0.80 per cent carbon steel is retained for a period of a few minutes in a nonmagnetic state after quenching in a molten salt bath. He investigated principally the recovery of magnetism in the steel on air cooling after the hot-bath

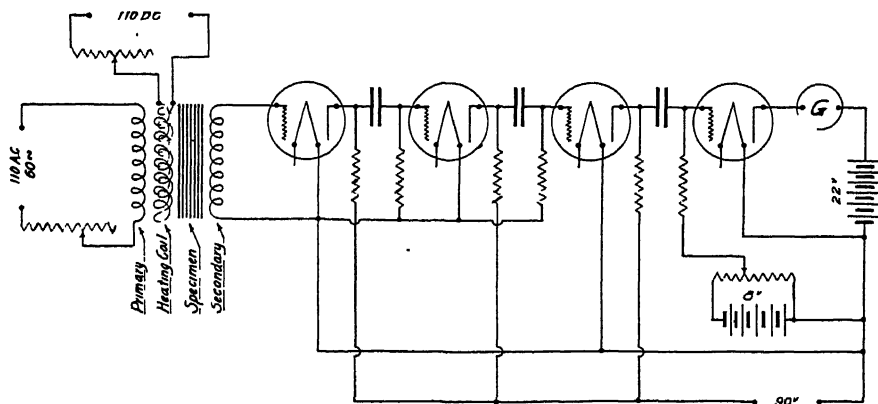


FIG. 1.—WIRING DIAGRAM OF THE APPARATUS.

quench. The thermal studies of the quenching process by French⁽⁵⁾ and by Esser and his coworkers⁽⁶⁾ were of great assistance in the present investigation.

APPARATUS

To study the magnetic transformations in steel during the quenching process required the construction of a suitable apparatus, since available methods for the thermomagnetic analysis were ill suited for the conditions existing during the quenching. The following requirements were considered necessary for a suitable apparatus:

1. The specimen should be as short as possible because the temperature was to be measured with a thermocouple at a single point. A long specimen is subject to uneven distribution of temperature and related magnetic changes during quenching. It was realized that the accuracy of magnetic measurements would be sacrificed with a short specimen, but the absolute magnetic values were considered of secondary importance.

2. Specimens should be as free as possible from the encumbering effect of necessary coils which would affect the rate of cooling during quenching.

3. The apparatus and recording devices should be of a low period, so as to respond to instantaneous magnetic and thermal changes during quenching.

The principal features of the apparatus¹ constructed to satisfy these requirements were as follows:

1. Employment of an alternating flux of 60 cycles per second.

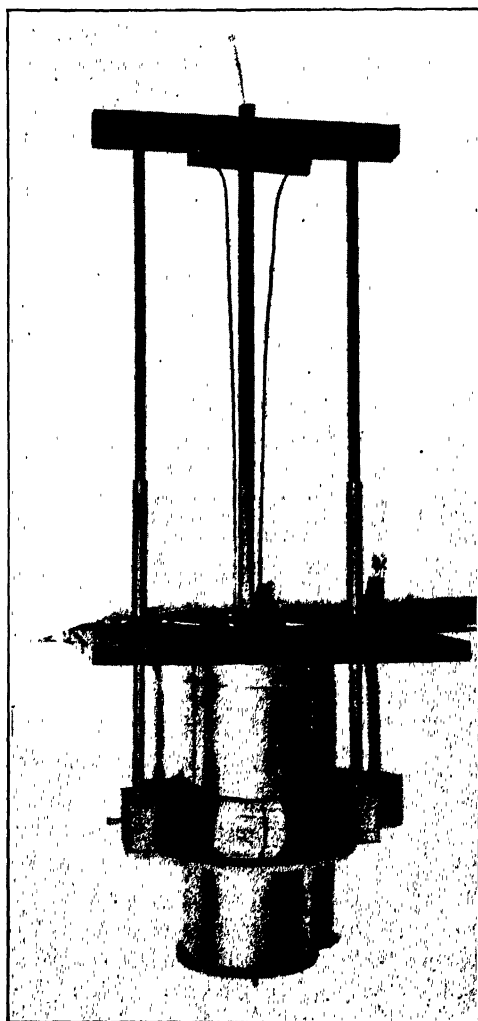


FIG. 2.—GENERAL VIEW OF FURNACE. NOTE THE PRIMARY COIL OUTSIDE THE FURNACE.

2. The use of a triod tube amplifier to raise the voltage induced in the detecting coil of the apparatus to a measurable degree.

¹ The apparatus thus constructed resembles in certain features one described by Houghton in the *Jnl. of Sc. Instr.* (1931) 8, 7. There is no record that Houghton designed or used his apparatus for quenching experiments. The author's apparatus was in operation at least two years previous to the appearance of Houghton's article.

3. The use of a d.c. galvanometer for measurement of the output of the amplifier when the apparatus was used for equilibrium runs.

4. The use of an oscillograph for quenching runs.

The details of the apparatus can best be illustrated by the diagram (Fig. 1) showing all electrical connections.

The primary coil, also shown outside the furnace in Fig. 2, consisted of 300 turns of No. 18 gage copper wire. The arrangement of the coil

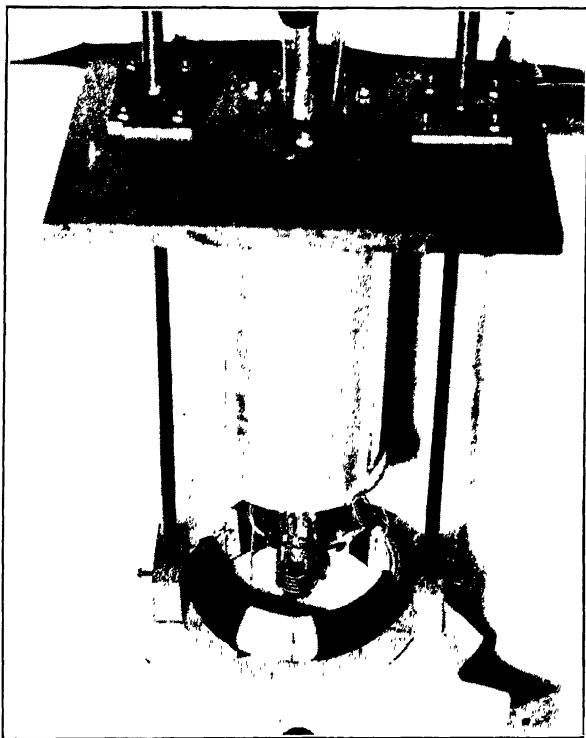


FIG. 3.—FURNACE AND COILS IN QUENCHING POSITION. PRIMARY COIL OUTSIDE THE QUENCHING BATH (BEAKER), SPECIMEN, AND THE SECONDARY COIL IN THE BATH.

was such as to allow it to remain cool during the heating of the specimen and dry during quenching (Fig. 3). The primary coil was connected to a 110-volt, alternating, 60-cycle line. Selection of low frequency for excitation of the flux received serious consideration. Little information is available on the behavior of iron alloys in the high-frequency flux at elevated temperature. Experiences of Regner⁽⁷⁾ with high frequencies seemed to justify the use of low frequencies in the present investigation.

The heating coil of the furnace was noninductively wound on an alundum tube 1.75-in. bore, 12 in. long. The long heating coil was considered necessary to insure uniform distribution of temperature throughout the specimen.

The secondary or detecting coil consisted of 4.5 turns of No. 8 constantan wire; it was situated inside the heating unit during heating and was quenched together with the specimen. The secondary coil was of sufficient dimensions to allow a free circulation of the quenching medium (Fig. 4). The primary and secondary coils and the specimen holder, together with suitable guides, formed a framework which insured their relative vertical movement with respect to the stationary furnace. The specimen and the coils were kept in the same relative position during heating or quenching.

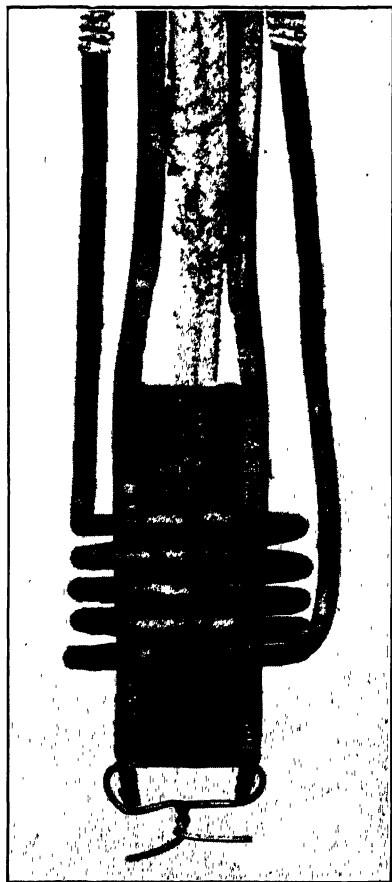


FIG. 4.—SPECIMEN USED IN EQUILIBRIUM RUNS, SPECIMEN HOLDER, AND THE SECONDARY COIL OF 4.5 TURNS.

The amplifier was a standard, resistance coupled, audio-type, three-stage amplifier, commonly used in radio circuits. All tubes used in the circuit were of UX-201-A type. The fourth tube was used as a rectifier for the d.c. galvanometer, when the apparatus was employed in the equilibrium runs.

The type of the temperature-magnetization curve obtained with the apparatus under conditions of equilibrium is shown in Fig. 5. The curve is characterized by a practically horizontal section up to the magnetic transformation point, then by a sharp break and quite a sharp ending of the vertical drop without appreciable rounding. The type of the curve thus obtained was obviously eminently suitable for the purpose of this investigation.

Quenching experiments required an oscillograph for recording the output of the amplifier and for recording the temperature of the specimen. French⁽⁵⁾ and Esser⁽⁶⁾ used a string galvanometer in their investigation of the quenching process. Two vibrators were required for the present investigation. The difficulties of operating string galvanometers are well known and certainly would multiply with an instrument provided with two vibrators instead of one. A suitable instrument was found in an oscillograph of Blondel type, having two vibrators whose characteristics are given in Table 1.

TABLE 1.—*Characteristics of the Oscillograph Vibrators*

Vibrator	Used in	Current per Inch Deflection, Amp.	Natural Freq., Cycles per Sec.	Resistance, Ohms
1	Thermocouple circuit	0.002	1300	8
2	Amplifier circuit	0.006	3000	8

A chromel-constantan thermocouple was eventually adopted in the following experiments. A chromel-alumel combination was found undesirable on account of a magnetic transformation in alumel at about 138° C. Noble thermocouples were not suitable because their e.m.f. was too low to operate the oscillograph vibrator.

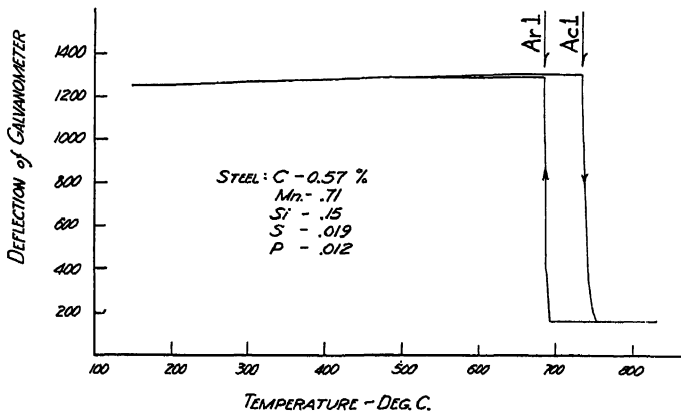


FIG. 5.—TYPICAL TIME-MAGNETIZATION CURVE OBTAINED UNDER EQUILIBRIUM CONDITIONS.

The size and the methods of attaching thermocouples to the specimen were next investigated. Welding of the thermocouples to the specimens was found to be the only suitable method. The difficulties of welding small thermocouples to the specimens with makeshift welding equipment forced adoption of relatively large wires, No. 14 gage (0.065 in.). These were welded to the samples in the manner illustrated in Fig. 6, the specimen itself forming the hot junction of the thermocouple.

In the present work, the author followed the example of French and of Esser in assuming that the temperature indicated by a thermocouple welded to the specimen represents the surface temperature of the specimen during quenching. It will be seen, in the light of the results presented later, that this fine distinction with respect to the exact temperature of the specimen during quenching is not so important for drawing the conclusions.

PRELIMINARY WORK

The preliminary work consisted of a series of experimental runs in which the magnetic transformation was studied under conditions generally termed as those of equilibrium. Their object was, first, to investigate the performance of the apparatus; second, to compare the results thus obtained with available results of other investigations; and finally, to draw conclusions with respect to the relationship between the magnetic and phase transformations in carbon steels heated and cooled under conditions of equilibrium.

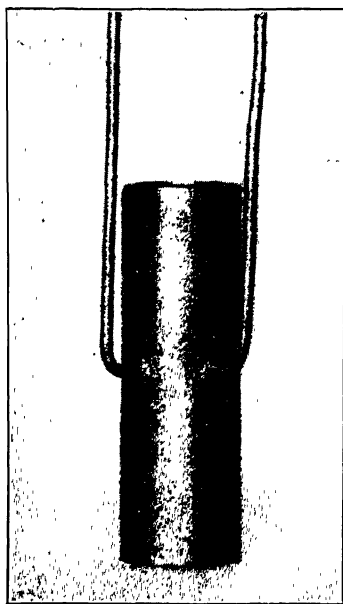


FIG. 6.—THERMOCOUPLE WIRES WELDED TO THE SPECIMEN FOR QUENCHING RUNS.

The results of the equilibrium runs can be summarized as follows:

1. The magnetic transformation point Ac_2 begins and ends distinctly above the Ac_1 point on heating steels containing 0.50 per cent or less of carbon. Point Ar_2 , on cooling, begins and ends distinctly above the phase transformation point Ar_1 for these steels.

2. The magnetic transformation Ac_2 , on heating steels containing 0.60 per cent or more carbon, starts and is practically completed at the temperature of the Ac_1 point, the end of the Ac_2 point occurring at a temperature only slightly above the Ac_1 point. On cooling, these steels exhibited a supercooling effect. The mag-

netic transformation point Ar_2 in steels containing 0.60 per cent or more carbon was invariably observed to begin at the bottom of the supercooling loop of the time-temperature curve and to end approximately in the middle of the Ar_1 transformation.

MATERIALS USED IN QUENCHING EXPERIMENTS

Time and facilities were not available for the preparation of iron-carbon alloys of high purity. The term "purity" in connection with iron alloys is a relative term. The iron-carbon diagrams in general use today are not based on data obtained with materials of extreme purity. The materials, therefore, for the experiments to be described were bought in the open market, and were in the form of $\frac{3}{4}$ -in. round or square bars. Composition of the materials used in quenching experiments is given in Table 2.

TABLE 2.—*Chemical Composition of Materials Used in Quenching Experiments*

Material	C	Mn	Si	S	P
Electrolytic iron.....	Not analyzed				
Armco iron.....	Not analyzed				
Steel.....	0.19	0.65	0.15	0.073	0.017
Steel.....	0.45	0.65	0.04	0.033	0.008
Steel.....	0.67	0.78	0.10	0.034	0.047
Steel.....	0.85	0.38	0.10	0.047	0.012
Steel.....	1.03	0.27	0.18	0.005	0.005
Steel.....	1.12	0.22	0.19	0.011	0.013
Steel.....	1.19	0.22	0.15	0.006	0.015

QUENCHING EXPERIMENTS

Preliminary experiments with solid specimens immediately showed that the magnetic transformation during quenching was spread over a considerable range of temperature, and a relatively long interval of time. It was thought at first that the observed phenomenon was due to the existence of a temperature gradient in the solid specimen during quenching, the presence of which, during quenching, had already been demonstrated by French.⁽⁵⁾ To minimize the gradient, the mass of the specimens was progressively diminished by drilling a larger and larger hole along the axis of round specimens. Drilling a hole also increased the surface subjected to the action of the quenching medium. Further experiments with tubular specimens showed very little difference compared with the solid specimens.

To settle the question as to the influence of the mass of the specimen on the spread of magnetic transformation over a range of temperature, an experiment was performed by quenching a specimen having a very small mass. The sample used in this experiment was a piece of iron thermocouple wire, of 0.064 in. diameter, $\frac{3}{4}$ in. long. The sample was welded on both ends to chromel and constantan thermocouple wires of the same diameter. With a velocity of quenching of about 6000° C. per second, it required about 0.125 sec. to complete the magnetic transformation with this sample. The spread between the beginning and the end of magnetic transformation was about 500° C. The experiment just described quite conclusively demonstrated that, with a specimen of very small mass and with high rates of quench, the magnetic transformation is spread over a considerable range of temperature and over a considerable interval of time. It was concluded, also, that no benefit could be expected from decreasing the mass of the specimen with the object of confining the magnetic transformation to a narrow range of temperature.

The specimens used for a series of quenching experiments described below were made in tubular shape, 2 in. long, $\frac{5}{8}$ in. outside diameter, with wall thickness of $\frac{1}{16}$ inch.

Quenching was carried out in the stationary bath. Tap water, de-aerated distilled water, and brine were all tested, but the first two were soon discarded as quenching mediums. Time-temperature cooling curves obtained with water as quenching medium showed certain well developed stops which could easily be accepted as the Ar'' points. Observation that they occurred at the same temperature and extended for the same length of time with electrolytic iron as with high-carbon steel led to the conclusion that the stops were caused rather by the quenching medium itself than by the evolution of heat due to the suppressed phase transformation. Magnetic changes were not related to these stops. A 20 per cent solution of sodium chloride in water was finally adopted as a quenching medium; the smooth cooling curves with this medium were free from any stops that could be mistaken for the depressed transformation points. Absence of the thermal indication of the phase transformation when using brine precluded the establishment of the relationship between the magnetic and the phase transformations in steels.

Another important observation must be recorded. A sample of steel, repeatedly quenched, showed the temperature at the beginning of magnetic transformation to be invariably higher on the second and following quenches than on the first quench. The data in Table 3 illustrate this point.

TABLE 3.—*Temperature at Beginning of Magnetic Transformation on Repeated Quenching*

Steel, Per Cent C	1st Quench	2d Quench	3d Quench
0.67	520	620	630
0.85	470	570	550
1.03	375	500	500

It was thought at first that the phenomenon was due to slight decarburization of specimens, notwithstanding illuminating gas protection during heating. But it was repeatedly observed that the second and the following quenches agreed reasonably well one with another but disagreed with the first. Agreement between the second and the following quenches apparently excludes decarburization as a possible cause of raising the beginning of the magnetic transformation.

The end of the magnetic transformation was not greatly affected by previous quenches. The observations here recorded were not further investigated at this time. For the reasons just stated, the data presented in Table 4 were obtained for originally annealed samples on the first quench.

Table 4 contains the results of quenching experiments with steels of which the chemical composition is given in Table 2. The conditions under which the data were obtained are specified, and the data of Table 4 are presented graphically in Fig. 7.

The terms "beginning" and "end" of magnetic transformation, as used in Table 4, need explanation. The changes in the magnetic state of the specimens were derived from measurement of the amplitude of the 60-cycle wave recorded on the oscillograms. With specimens of carbonless iron or with low-carbon steel, the changes in the amplitude at the beginning and end of magnetic transformation were sharp and definite. With medium or high-carbon

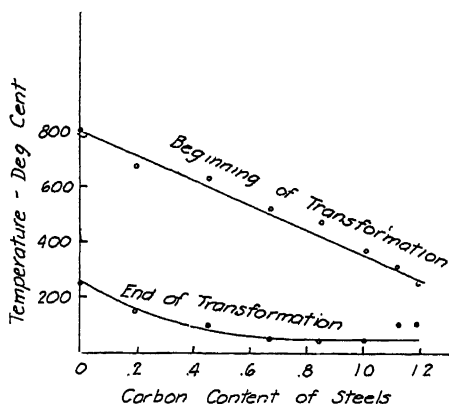


FIG. 7.—BEGINNING AND END OF MAGNETIC TRANSFORMATION IN CARBON STEELS ON BRINE QUENCHING.

TABLE 4.—Data on Quenching Tests

Material	Carbon, Per Cent	Beginning of Transformation, Deg. C.	End of Transformation, Deg. C.
Electrolytic iron.....		800	250
Armco iron.....		800	150
Steel.....	0.19	675	150
Steel.....	0.45	630	100
Steel.....	0.67	520	50
Steel.....	0.85	470	50
Steel.....	1.03	375	50
Steel.....	1.12	310	100
Steel.....	1.19	250	100

EXPERIMENTAL CONDITIONS

Alternating flux of 60 cycles per second. Induction about 200 gaussess.

Specimens in form of tubes, $\frac{5}{8}$ in. outside diameter, 2 in. long, $\frac{1}{2}$ in. bore, $\frac{1}{16}$ in. wall thickness.

Chromel-constantan thermocouple welded to the specimen.

Quenching medium stationary solution of 20 per cent NaCl.

All specimens quenched from initial temperature of 950° C.

Specimens protected from scaling with illuminating gas.

Rate of cooling for temperature drop from 800° to 700° C. (Esser's method), 750° C. per second.

Data in the table relate to the first quench.

quite readily detectable, but its end was not easily discernible. The amplitude of the 60-cycle wave increased in these steels from the "beginning" of the transformation almost proportionately with drop in temperature; then at the "end" of the transformation the rapid rate gradually changed to a very slow one. Under these conditions, the "end" of the magnetic transformation, as recorded in Table 4, signifies a temperature at which a rapid rate of magnetic recovery changed to a relatively slow one. It was apparent from examination of oscillograms that the "end" of the magnetic transformation is a relative point. The magnetic aging effect was apparent in the oscillograms for a period of a few seconds after completion of quenching. Magnetic aging effect in quenched steel is known to proceed for days, weeks, and even months.

DISCUSSION

Determination of the magnetic transformation in carbon steels under conditions of equilibrium leads to the conclusion that a close association of magnetic transformation with the phase transformation exists only for steels containing 0.60 per cent or more carbon. In carbon steels containing less than 0.60 per cent carbon, the magnetic transformation is independent of the phase transformation under conditions of equilibrium. The relation, if such exists, between the magnetic and phase transformations is limited to a certain group of carbon steels. Examination of the available data for alloy systems of iron with elements other than carbon shows also a lack of relationship between the magnetic and phase transformations under conditions of equilibrium. Available diagrams, for example, for alloys of iron and vanadium,⁽⁸⁾ iron and chromium⁽⁹⁾ and of iron and molybdenum⁽¹⁰⁾ show a wide divergence between the magnetic transformations and the gamma-phase loops.

The quenching experiments described above were carried out at velocities of quench far in excess of those necessary to retain the samples in a martensitic state. It was found that, under these conditions, the magnetic transformation is not confined to a single temperature or to a narrow range of temperature, but extends over a considerable range. Cooling curves obtained during brine quenching with thermocouples welded to the specimens failed to show the thermal arrests that are usually taken for the temperatures of the phase transformations. Comparison of the results here presented with data of Esser (who also used surface temperature in his experiments) justifies the conclusion that the magnetic transformation is not related to phase transformation during quenching. The spread of the magnetic transformation over a considerable range of temperature should constitute sufficient evidence of the lack of relationship between the magnetic and phase transformations in carbon steels during quenching.

SUMMARY

1. An apparatus is described suitable for the study of magnetic transformation in steels under conditions of equilibrium as well as during quenching.

2. A summary of equilibrium runs with carbon steels is presented. It is shown that close association between the magnetic and the phase transformations exists only for steels containing 0.60 per cent or more carbon. Magnetic transformation is not related to the phase transformation for steels containing less than 0.60 per cent carbon.

3. Quenching experiments with carbon steels are described. It was found, with rates of quenching far in excess of those necessary for the formation of martensite, that the magnetic transformation is not confined to a single temperature or to a narrow range of temperature but is spread over a considerable range of temperature and over a considerable interval of time. The beginning and the end of magnetic transformation was obtained for certain quenching conditions.

4. Direct evidence of the relationship between the phase and the magnetic transformations, or lack of such relationship, during quenching was not experimentally established, but the discussion brought out lack of such relationship.

ACKNOWLEDGMENT

The author wishes to express his thanks to the Department of Mining and Metallurgy of the Massachusetts Institute of Technology for the facilities placed at his disposal in carrying out this work; also to Dr. Robert S. Williams for his help and constant encouragement of the work here presented.

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Studies upon the Widmanstätten Structure, V—The Gamma-alpha Transformation in Pure Iron

BY ROBERT F. MEHL* AND DANA W. SMITH,† PITTSBURGH, PA.

(New York Meeting, February, 1934)

It has been shown that quenched iron of high purity exhibits a Widmanstätten figure much resembling martensite in appearance.¹ This figure exhibits a maximum of four directions of the surface traces that characterize it, suggesting that α Fe forms from γ Fe in plates parallel to the $\{111\}$, octahedral, planes in the γ lattice. Because of this, and also because of the general similarity to the structural appearance of martensite and to the Widmanstätten figure obtaining in slowly cooled hypoeutectoid steels it has been suggested² that the orientation relationships obtaining between the γ and α phases in pure iron are identical with those demonstrated in martensite³ and in slowly cooled hypoeutectoid steels,⁴ and indeed that the crystallographic mechanism of formation of α Fe from γ Fe is the basic mechanism determining the orientation relationships found in both martensite and in slowly cooled hypoeutectoid steels. This paper will present experimental evidence in support of this view.

EXPERIMENTAL TECHNIQUE

The analysis of the crystallographic mechanism of transformation in pure metals is beset with special difficulties, though some information

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¹ A. Sauveur and C. H. Chou: The Gamma-alpha Transformation in Pure Iron. *Trans. A. I. M. E.* (1929) **84**, Iron and Steel, 350.

F. Osmond: *Sur la Cristallographie du Fer*, 24. Paris, 1900.

² R. F. Mehl, C. S. Barrett and D. W. Smith: Studies upon the Widmanstätten Structure IV—The Iron-carbon Alloys. *Trans. A.I.M.E.* (1933) **105**, Iron and Steel, 215–258.

³ G. Kurdjumow and G. Sachs: Über den Mechanismus der Stahlhärtung. *Ztsch. f. Phys.* (1930) **64**, 325–343.

⁴ R. F. Mehl, C. S. Barrett and D. W. Smith: Reference of footnote 2.

has been obtained for the transformations⁵ in Co and Ti. When the transformation takes place at a high temperature a determination of the orientation of single crystals of the phase stable at the higher temperatures is necessary but difficult by direct means; furthermore, the growth of the new phase at the transformation temperature is likely to be so rapid that relatively few crystals of the new phase are available for analysis, and when formed from an aggregate of grains of the high-temperature form, the identity of the grain from which any new crystal forms is uncertain. In addition, the great plasticity of pure metals, especially at high temperatures, permits a wide shifting of orientations during the transformation by reason of the accompanying volume change and resultant grain distortion and movement.

The technique involved in the present work was designed to evade these difficulties. The orientation of an original γ Fe grain was obtained by a measurement on two surfaces of polish of the trace directions in the martensitlike structure obtained by quenching from above the transformation temperature following a technique similar to that used by Sauveur and Chou. The continuity of the figure obtained and the etching properties of the sample served to identify the limits of one original γ Fe grain. This grain was then subjected to a pole-figure analysis somewhat similar to that used for preferred orientations and that applied by Kurdjumow and Sachs (*loc. cit.*) to the analogous case of true martensite, and from this analysis, and the indirectly determined orientation of the parent γ -Fe grain, the crystallographic relationships obtaining between the two phases was derived.

A special grade of electrolytic iron, prepared by the United States Bureau of Printing and Engraving and subsequently purified by heating in a stream of undried hydrogen for 93 hr. at 1200° C., was used for this work. After purification this iron showed the following composition: C, 0.004 per cent; Mn, 0.002; P, 0.001; S, 0.004; Si, 0.002; Cu, 0.005; Ni, 0.009; Cr, 0.008; O, 0.003.

Samples of this iron were suspended on the end of a heavy rod in a vertical tube furnace in a slowly flowing stream of tank hydrogen and maintained at a temperature of 1300° to 1350° C. for periods varying from 3 to 12 hr., in order to grow large grains without destructive oxidation. At the end of this period the temperature was dropped to 950°–1100° C., and the specimen driven rapidly by the fall of the rod into a tube quenching chamber with a high-pressure radial spray of water.

⁵ G. Wassermann: Über die Umwandlung des Kobalt. *Metallwirtschaft* (1932) 11, 61–65.

U. Dehlinger: Über den Mechanismus der allotropen Umwandlung von Kobalt und Thallium, *Metallwirtschaft* (1932) 11, 223–235.

U. Dehlinger, E. Osswald and H. Bumm: Über die Umwandlung von Kobalteinkristallen. *Ztsch. f. Metallkunde* (1933) 25, 62–63.

The object of this treatment was to produce a very rapid quenching action, for experience showed this to be necessary for the development of a Widmanstätten figure. The specimens were approximately 1.6 cm. long, 1.0 cm. wide, varying in thickness from 0.25 to 0.025 cm.; the thickness of the piece proved of great importance, for with thick pieces no figure was developed and with thin warping was so severe that the specimen could not be used. Pieces were chosen thin enough to develop well formed figures but not so thin as to warp. Despite a large number of runs, the optimum quenching temperature and the optimum specimen size for the apparatus used cannot be given. Success was sporadic and



FIG. 1.

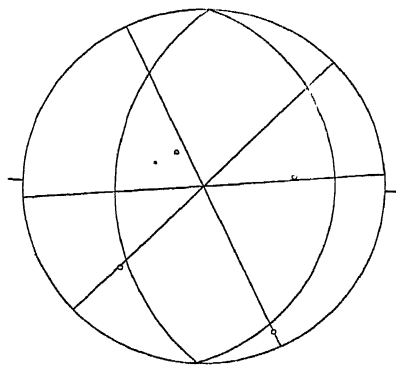


FIG. 2.

FIG. 1.—WIDMANSTÄTTEN FIGURE IN QUENCHED PURE IRON. $\times 85$. ETCHED WITH 4 PER CENT NITAL AFTER POLISHING.

FIG. 2.—STEREOGRAPHIC PROJECTION OF WIDMANSTÄTTEN FIGURE SHOWN IN FIG. 1. DIAMETERS REPRESENT NORMALS TO TRACES ON FIRST SURFACE; GREAT CIRCLES REPRESENT NORMALS TO TRACES ON SECOND SURFACE PROJECTED UPON FIRST SURFACE; CIRCLES REPRESENT POSITIONS OF $\{111\}$ POLES THAT ACCOUNT FOR THE TRACES.

unpredictable, yet nevertheless a few examples of satisfactory structures were obtained.

The grain chosen for analysis was approximately 2 mm. long, 1 mm. wide, extending through the thickness of the specimen, 0.063 cm. The Widmanstätten figure developed is shown in Fig. 1.

DETERMINATION OF PLANE OF PRECIPITATION

This grain was cut and polished on two sides. The traces upon one side, the flat side of the specimen, were accurately measured and the normals to these traces plotted as diameters on a stereographic projection, Fig. 2. It was found that $\{111\}$ poles could be rotated so that one pole fell on each of the normals to the traces. Since, however, there are two orientations of the $\{111\}$ poles showing this coincidence, related to each other as object and mirror image, it is necessary to procure other data to determine the unique orientation. This was done

by making a measurement of the directions of traces on the second surface, which stood at 90° to the first, or "flat surface," and plotting normals to these directions as great circles on the projection, Fig. 2. The points of intersection of the diameters and the great circles gives the proper selection of the two solutions; this orientation is represented by four $\{111\}$ poles shown as circles on Fig. 2. The traces on the second surface could not be accurately measured because of the thinness of the specimen, and for this reason the intersections do not fall accurately upon the plotted $\{111\}$ poles. The positions of the $\{111\}$ poles, however, are more precise than might be suspected from this, since the traces on the second surface were used only to determine the proper selection of the alternative solutions, while the precise positions of the $\{111\}$ poles were determined by rotation into the most satisfactory coincidence with the diameters.

The coincidence shown is proof that the martensitic markings in the specimen formed parallel to the $\{111\}$, octahedral, planes in the γ -Fe grain. This, then, is quantitative confirmation of the semiquantitative observations of Sauveur and Chou.

DETERMINATION OF ORIENTATION OF α PHASE

The selected grain was mounted in the path of a beam of polychromatic or "white" X-rays from a tungsten target, and photograms taken at a series of angular positions of the surface of the grain with respect to the X-ray beam. This technique differs from the usual pole-figure technique in the use of polychromatic rays instead of characteristic rays; it involved the measurement upon the photogram of the angular positions of intensity maxima of diffracted rays of wave length between the low wave length limit as determined by the voltage applied to the X-ray tube and the wave length corresponding to the absorption limit of the silver emulsion in the photographic film. Some advantages accrue to this technique; for instance, a wider range of orientations was registered upon each photogram, a matter of some importance in view of the labor involved in obtaining a full pole-figure in a system showing as much scatter in orientation as the one under observation.⁶

Twenty-one photograms were taken, ten in 5° intervals on each side of the position in which the specimen stood perpendicular to the X-ray beam, thus covering an angular range of 100° . The reflection maxima, like those shown in Fig. 3, originated in diffraction of the polychromatic X-ray beam from the $\{110\}$ planes in the α crystals, since these have the greatest $d_{(hkl)}$ value and thus lie closest to the zero or beam position on the photogram. These maxima were plotted upon a stereographic

⁶ We are indebted to Dr. Charles S. Barrett of this laboratory for suggesting this method.

projection, Fig. 4, upon which were also plotted the positions of the $\{111\}$ poles of the original γ lattice previously determined.

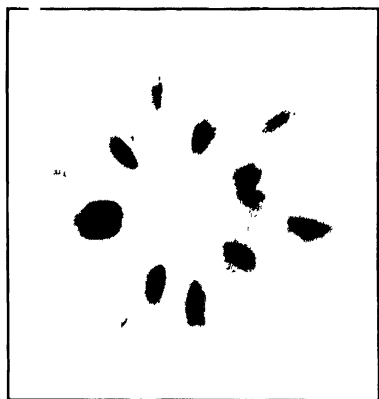


FIG. 3.

FIG. 3.—TRANSMISSION X-RAY PHOTOGRAPH OF SPECIMEN. SURFACE OF SPECIMEN AT 20° TO DIRECTION OF X-RAY BEAM.

(The original photographs show detail within the reflection maxima.)

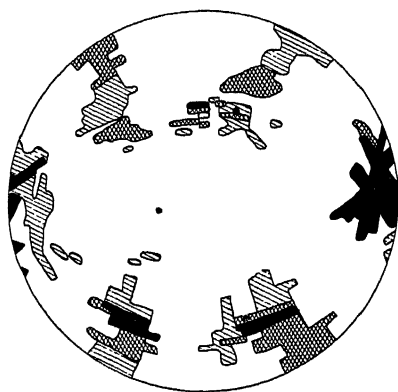


FIG. 4.

FIG. 4.—POLE-FIGURE OF $\{110\}$ α PLANES. SURFACE OF PROJECTION IS THAT OF THE FIRST SURFACE.

In order to concentrate the data, since but 114° of the full 180° angular range was studied, the areas and poles in Fig. 4 were rotated so as to bring the $\{111\}$ poles into the positions they occupy in a standard cubic projection, and further rotated into one quadrant, Fig. 5.

The mechanism of transformation in martensite and in slowly cooled hypoeutectoid steels may be described crystallographically by the symbols:

$$\begin{array}{l} \{111\}\gamma\parallel\{110\}\alpha \\ [110]\gamma\parallel[111]\alpha \end{array}$$

which specifies the planes in the two lattices that lie parallel and also the directions in each of these planes that lie parallel. This specification calls for a total of 24 orientations of the α Fe with respect to each single orientation of γ Fe. These ideal orientations are represented by black dots in Fig. 5.

In plotting the intensity maxima from the photographs, an attempt was made to distinguish three degrees of intensity. These are represented in Fig. 5 by the variously shaded areas.

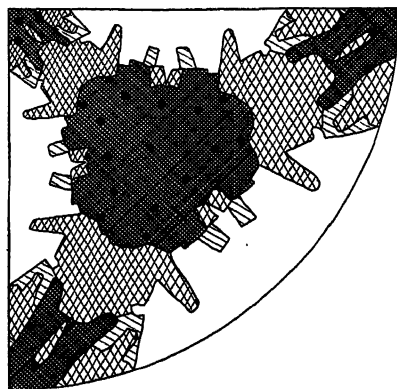


FIG. 5.—POLE-FIGURE OF $\{110\}$ α PLANES ROTATED INTO ONE QUADRANT OF STANDARD PROJECTION.

Fig. 5 shows that the poles of the $\{110\}$ planes fall in areas in the neighborhood of those predicted by the crystallographic relationship stated above. The coincidence is not nearly so good as that obtained by Kurdjumow and Sachs for martensite in quenched high-carbon steels, but is probably as good as can be obtained, in view of the great plasticity of the iron while suffering the volume change and in view of the gross distortion accompanying the quenching operation. The centering of the pole areas around the predicted positions and the lack of any consistent and important indication of other positions leaves little or no doubt that the crystallographic relationships between the γ and α lattices are those specified above.

DISCUSSION OF RESULTS

It seemed clear from the evidence obtained in the study of martensite and of the Widmanstätten figure in slowly cooled hypoeutectoid steels that pure iron must show a crystallographically identical behavior. Such, indeed, will doubtless often be found in alloys in which transformations occur that find their origin in allotropic transformations; in such cases the orientation relationships in the alloys may often be predicted from those determined for the allotropic transformation in the pure metal and vice versa. If, however, solid solution formation in the participating phases alters lattice dimensions greatly it is quite possible that increasing solid solution formation may see the initiation of a new and separate crystallographic process as new and preferable lattice transformation mechanisms become possible. In the steels carbon alters the dimensions of γ iron only slightly, and α Fe dissolves but little carbon with an inappreciable alteration in its dimensions, and thus a common mechanism is preferable for both steels and pure iron. The apparent change in the crystallographic mechanism of the precipitation of CuAl_2 from the solid solution of Cu in Al upon increasing Cu content may be an example of the effect of changes in lattice dimensions, in this case upon a mechanism greatly sensitive to a change in lattice dimensions.⁷

SUMMARY

1. The Widmanstätten figure in drastically quenched pure iron delineates the $\{111\}$, octahedral, planes in γ iron.
2. An analysis of the orientations of the α phase with respect to the parent γ phase shows a satisfactory agreement with the relationships previously found in martensite and slowly cooled hypoeutectoid steels; to wit:

⁷ R. F. Mehl, C. S. Barrett and F. N. Rhines: Studies upon the Widmanstätten Structure, III. *Trans. A.I.M.E.* (1932) **99**, 203-233.

$$\begin{array}{l} \{111\}\gamma \parallel \{110\}\alpha \\ [110]\gamma \parallel [111]\alpha \end{array}$$

in which the directions indicated lie in the planes indicated.

3. It is suggested that the orientations obtaining in Widmanstätten figures in alloys, which are made possible by an allotropic transformation in the pure metal, will be identical to those found for the allotropic transformation in the pure metal, when solid solution formation does not so greatly change the lattice dimensions as to make a different transformation mechanism preferable.

DISCUSSION

(F. B. Foley presiding)

M. A. GROSSMANN,* South Chicago, Ill.—A good deal of the interest and importance of the portion of this series hinges on the completeness with which the 24 different orientations are actually found. I wonder if Dr. Mehl would be willing to say a word or two on that point?

U. DEHLINGER,† Stuttgart, Germany (written discussion).—It would be interesting to know whether the gamma-alpha transformation in pure iron is accompanied by the hysteresis we have recently studied in the iron-nickel system.[§] On cooling from high temperatures to very low ones, crossing the heterogeneous field $\alpha + \gamma$ very rapidly, we have found that the transformation into α takes place by a shearing process alone, without any precipitation in the ordinary sense, and produces a very symmetrical Widmanstätten figure. However, the transformation of α into γ on subsequent heating does not begin until a temperature is reached several hundred degrees higher than that of the beginning of the transformation of γ to α on cooling. We have suggested that the displacement to lower temperatures of the transformation of γ to α is caused by lattice distortions accompanying the first lattice shear. Since these distortions are roughly independent of the nickel content, a similar hysteresis is to be expected in pure iron also.

R. F. MEHL (written discussion).—The work reported in this paper does not furnish an answer to Dr. Grossmann's question. It has merely been shown that each gamma crystal can produce alpha crystals exhibiting 24 different orientations. There is no requirement that each gamma crystal must produce all of the 24 orientations, or that there should be only one alpha crystal for each of the 24 orientations. The number of alpha crystals may vary from one to an infinitely large number. The number of crystals formed will depend on such factors as speed of cooling and the composition of the iron both with respect to alloy content and inclusions. Dr. Grossmann's own studies on this latter point have furnished us with much valuable information.

I have just read Dr. Dehlinger's paper on the transformations in iron-nickel alloys. The problem of irreversibility in alloys of this sort, of which there are several, is very puzzling. Evidently, as Dr. Dehlinger points out, strains accompanying the first shearing action inhibit further transformation. The many studies of the mar-

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† Röntgenlaboratorium an der Technischen Hochschule.

§ U. Dehlinger: Kinetik und Zustandschaubild der irreversiblen Umwandlung im System Eisen-Nickel. *Ztsch. f. Metallkunde* (1934) **26**, 112-116.

tensite transformation in steels have furnished good evidence on this point. It is quite clear now that the rates of transformation just below the critical temperatures shortly reach a maximum, then at lower temperatures a minimum owing to a slowing up of the diffusion process, and at still lower temperatures begin to attain very high values since an entirely different process sets in; namely, one of pure shear without diffusion. This has been amply proved by the numerous studies by Bain, Wever, and others. Iron-nickel alloys are another example of this type of behavior. The rate curve which Dr. Dehlinger shows in Fig. 4 in the paper he quotes is exactly similar in type to those published by Bain.

Similar processes of pure shear unaccompanied by diffusion and therefore segregation have been shown in nonferrous alloys. The structures shown by Phillips⁹ for a quenched copper-zinc alloy wholly within the β field at a high temperature and wholly within the α field at a low temperature are evidently structures which form by a shearing mechanism alone.¹⁰ I should point out that the importance of the shearing movement of atom layers in such processes was suggested by Mehl and Barrett¹¹ at the same time that the suggestion was made independently by Kurdjumow and Sachs.

The question of hysteresis in the γ - α transformation in pure iron is less certain. Dilatometric curves, taken by Dr. Wells in my laboratory on iron of unusually high purity at a very slow cooling rate, $\frac{1}{8}^{\circ}$ per minute, show a difference between the beginning of the transformation on heating and the beginning on cooling of only 1° , which is at about the limit of accuracy of measurement. I doubt very much, therefore, whether there is any true hysteresis in the transformation of γ to α iron and the reverse transformation. This work will shortly be published.

⁹ A. J. Phillips: The Alpha-beta Transformation in Brass. *Trans. A.I.M.E.* (1930) **89**, 196.

¹⁰ See discussion by R. F. Mehl, preceding reference.

¹¹ R. F. Mehl and C. S. Barrett: Studies upon the Widmanstätten Structure, I—Introduction. The Aluminum-silver and the Copper-silicon Systems. *Trans. A.I.M.E.* (1931) **93**, 78.

Studies upon the Widmanstätten Structure, VI—Iron-rich Alloys of Iron and Nitrogen and of Iron and Phosphorus

By ROBERT F. MEHL,* CHARLES S. BARRETT,† PITTSBURGH, PA. AND H. S. JERABEK,‡ MINNEAPOLIS, MINN.

(New York Meeting, February, 1934)

THE precipitation of the nitride Fe_4N from the solid solution of nitrogen in α Fe and of the phosphide Fe_3P from the solid solution of phosphorus in α Fe both lead to the formation of structures that may be easily identified as Widmanstätten figures, within the meaning of the term as used in this series of papers. A complete solution has been obtained for the figure formed by Fe_4N . The structure of Fe_3P , however, is not fully known and a complete solution of this figure thus cannot be obtained; nevertheless, a study of this figure has furnished some new information.

PRECIPITATION OF Fe_4N FROM ALPHA SOLID SOLUTION OF N IN ALPHA Fe *Constitution of System Iron-nitrogen*

A knowledge of the constitution of the whole of the Fe-N system is unnecessary for this work, though the recent studies by Eisenhut and Kaupp¹ and by Lehrer² have clarified most of the moot points; it is sufficient for our purpose to state that α Fe of high purity dissolves 0.42 per cent of nitrogen in solid solution at the eutectoid temperature, 591° C., and that this solubility decreases at first rapidly and then more slowly until at room temperature the solid solubility amounts to approximately 0.1 per cent nitrogen.³

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‡ School of Mines and Metallurgy, University of Minnesota.

¹ O. Eisenhut and E. Kaupp: The System Iron-Nitrogen. *Ztsch. f. Elektrochemie* (1930) **36**, 392.

² E. Lehrer: Magnetic Studies on the System Iron-Nitrogen. *Ztsch. f. Elektrochemie* (1930) **36**, 460.

³ Data were taken from the work of Eisenhut and Lehrer, *loc. cit.*, which seems the most trustworthy; absolute solubility values are of little importance in this work.

The constitution diagram indicates that upon cooling this solid solution will precipitate the phase Fe_4N . Some doubt of the correctness of this had been previously expressed by two of the present authors,⁴ and considerable effort has since been expended to obtain unambiguous proof. Although such uncertainty may seem unnecessary in view of the certain knowledge of the constitution of the system in this range of composition, it seemed possible that the special atomic processes that lead to the formation of Widmanstätten figures might exert some special influence in determining the composition of a precipitating phase. In any event, careful work requires a proof of the composition of a precipitating phase since the argument for the atomic mechanism of precipitation depends upon a knowledge of the space lattice of the precipitate and thus requires identification of the precipitate.

It is possible that the previous conclusion that the precipitate is Fe_3N rather than Fe_4N was in error by reason of contamination of the sample with Fe_3N formed on the outer surface or along the grain boundaries; though care was taken to prevent contamination, the relative activity of attack of Fe_4N and Fe_3N by the nitric acid used in isolating the nitride is such that the residue from the nitric acid attack upon a mixture of Fe_4N and Fe_3N would be relatively enriched in Fe_3N . This difficulty was avoided by nitriding samples of Armco iron (previously purified by long treatment in hydrogen at high temperatures) in ammonia-hydrogen mixtures of such composition and at such temperatures that no primary Fe_3N could form. The equilibrium data given by Lehrer⁵ show that no primary Fe_3N will form at the nitriding temperature of 500° in ammonia-hydrogen mixtures with less than 57 per cent ammonia; thus in an experiment to prove the true identity of the precipitating phase the hydrogen-purified Armco iron was treated in an ammonia-hydrogen mixture with the percentage of ammonia kept below 50 per cent, under which conditions only the gamma phase, Fe_4N , and the alpha solid solution could form as primary products.

The nitride recovered from this iron by treatment in nitric acid, with precautions taken to procure only the nitride precipitated within the separate large grains, showed upon an X-ray powder diffraction photogram the characteristic lines of the Fe_4N phase only. The Widmanstätten figure exhibited was identical in outward appearance with those obtained under less restricted nitriding conditions, and the nitride plates were found to lie parallel to the same planes in α Fe; therefore it seems certain that in both cases the phase precipitating from the alpha solid solution is Fe_4N .

⁴ R. F. Mehl and C. S. Barrett: Some Observations on the System Iron-Nitrogen *Metals & Alloys* (1930) 1, 422-423.

⁵ Reference of footnote 2.

Formation and Outward Form of Precipitate

All of the structures studied were prepared from hydrogen-purified Armco iron nitrided at temperatures below the eutectoid temperature and subsequently slowly cooled. No study was made of the most favorable conditions for the formation of a well defined structure, since it is an easy matter in this case to obtain sufficiently well developed structures.

It has been pointed out that the "needlelike" structure obtained represents the formation of a phase in plate form along some plane in the alpha solid solution matrix.⁶ The customary designation of "needle"



FIG. 1.—TYPICAL NITRIDE "NEEDLE" STRUCTURE. DECARBURIZED MILD STEEL NITRIDED IN AMMONIA. $\times 500$.
Etched with picric in alcohol.

has caused no mischief in this case, for it is generally recognized that the needle represents the section of plate formed by the plane of polish. Observations made in the present work which show the continuity of such a needle around a 90° edge may serve to remove any remaining doubt on this score.

These "needles" are usually lenticular in shape, probably because of progressive growth from an original platelike nucleus (Fig. 1).⁷ High magnification does not resolve them into a complicated structure such as that found for Fe_3C plates precipitating from austenite, or such as that reported later for Fe_3P plates. The phase seems to be uniform

⁶ R. F. Mehl and C. S. Barrett: Reference of footnote 4.

W. Köster: The Problem of Nitrogen in Technical Iron, *Archiv f. d. Eisenhüttenwesen* (1930) **3**, 637.

⁷ R. F. Mehl and C. S. Barrett: Discussion. *Trans. A.I.M.E.* (1931) **93**, Inst. Metals Div., 120-121.

in structure, each plate a single crystal (see Figs. 5 and 6 also); X-ray photograms of separate plates, described later, confirmed this observation.

Crystallography of Participating Phases

The solid solution of nitrogen in α Fe is, like α Fe itself, body-centered cubic in structure. Eisenhut and Kaupp⁸ found nitrogen to increase a_0 , the side of the unit body-centered cube, from 2.860 for pure iron to 2.876 for a sample containing 0.42 per cent nitrogen. This difference is not great, and since the samples prepared in this study contained less nitrogen (for they were prepared at lower nitriding temperatures) and since high precision in this value is not necessary for the required comparisons of lattices, the value for pure iron, $a_0 = 2.86$, will be used.

The structure of the compound Fe_4N has been studied by Hägg.⁹ The iron atoms are arranged in a face-centered cubic structure, with the single nitrogen in the unit cell probably situated at the center of the cube; the uncertainty in the position of the nitrogen atom apparently need not concern us here, since previous work indicates that only the positions of the atoms of the element forming the solvent in the parent solid solution need be considered. According to Hägg, the side of the unit cube in Fe_4N is 3.789 Å.

Determination of Plane of Precipitation

The technique used here was similar to that employed previously in this series of papers. Three separate determinations were made, in each case upon separately prepared specimens. The first determination consisted in the preparation of a frequency curve of the directions of the traces of the nitride plate in a single large grain of the alpha matrix, prepared by nitriding a decarburized mild steel sample that contained very large grains (Fig. 1), and plotting upon a stereographic projection the normals to the average angular positions read from the frequency curve. Upon this projection the poles of the important low indices planes of the matrix, as found by an X-ray determination of the orientation of the alpha matrix, were plotted. These poles should lie upon or very near to the normals without exception. Fig. 2 shows one of the four plots (for four different alpha crystals) obtained in this way; 283 traces were measured in obtaining the frequency curve and the resultant normals. Evidently we are dealing with a 12-family plane, near to or identical to the $\{210\}_{\alpha \text{ Fe}}$. Since the poles of the nitride plates are not obtained in this method, the proof it furnishes of the $\{210\}_{\alpha \text{ Fe}}$ plane is not so rigorous

⁸ Reference of footnote 1.

⁹ G. Hägg: X-ray Studies on the Binary Systems of Iron with Nitrogen, Phosphorus, Arsenic, Antimony, and Bismuth. *Nova Acta Regiae Societatis Scientiarum Upsaliensis* [IV] (1929) 7, No. 1; X-ray Studies on the Nitrides of Iron. *Zisch. f. phys. Chem.* (1930) 8, 455.

as desired; it may be considered, however, that the method furnishes proof of the operation of a 12-family plane, and indicates that this plane is the $\{210\}_\alpha$.

In order to obtain the poles of the nitride plates and to compare their positions with the poles of the planes in the alpha lattice, samples containing large grains with suitable nitride structures were polished on two sides while a sharp edge was maintained; nitride plates that could be traced continuously around this edge were chosen for measurement, and the angles formed by each plate with the edge measured, sufficing to place the position of the plate in space and thus to fix its pole. Subsequently the orientation of the alpha matrix was determined by X-rays and the stereographic projection of this orientation superimposed upon that representing the positions of the poles of the nitride plates.

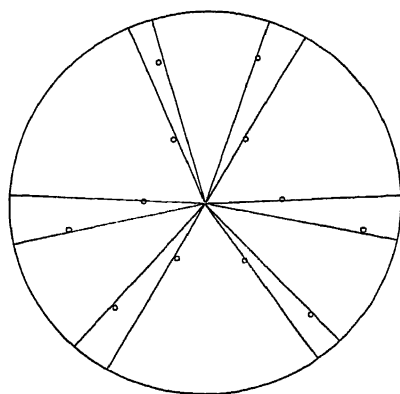


FIG. 2.—STEREOGRAPHIC PROJECTION OF DIRECTIONS TAKEN BY NITRIDE NEEDLES.

Radii represent normals to the maxima on the direction frequency curves. Circles represent locations of $\{210\}$ poles as determined by X-rays.

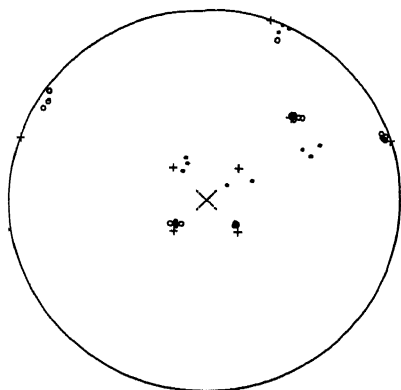


FIG. 3.

FIG. 3.—STEREOGRAPHIC PLOT OF POLES OF NITRIDE PLATES IN COMPARISON WITH POLES OF ALPHA IRON MATRIX. FIRST DETERMINATION.

Large circles show poles of nitride plates, positions of which could be accurately measured; dots show poles of nitride plates, positions of which could not be accurately measured; crosses show the $\{210\}_\alpha$ Fe poles.

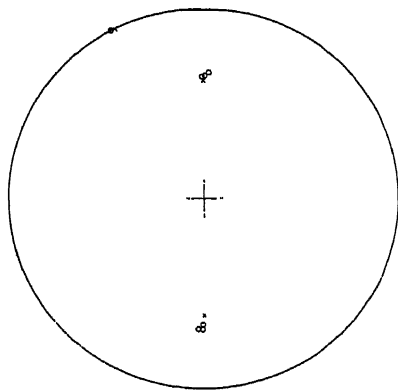


FIG. 4.

FIG. 4.—SIMILAR TO FIG. 3. ONLY ACCURATELY DETERMINED POLES OF NITRIDE PLATES ARE SHOWN. SECOND DETERMINATION.

The first determination was performed upon a large grain containing a suitable structure prepared by nitriding in pure influent ammonia a sample of Armco iron previously purified by treatment with hydrogen

at a high temperature. The resulting combined stereographic projection is shown in Fig. 3. Most of the nitride poles fall near to the $\{210\}$ poles; one group fell nearer the $(\bar{5}10)$ pole, but these were plates that made acute angles with the edge, and their positions therefore suffered in accuracy of determination because of the unavoidable slight rounding of the edge.

The second determination was made upon a similar type of sample but one nitrated under controlled conditions so that only primary Fe_4N could form. The combined stereographic projection for this sample is shown in Fig. 4. The coincidence of the plate poles with the $\{210\}$ poles is good. The data point consistently to the $\{210\}$ poles and only sporadically to other poles.

There can be no reasonable doubt from these data that the Fe_4N plates form from the solid solution of nitrogen in alpha Fe parallel to the $\{210\}$ planes.

Orientation of Fe_4N Plates

Since it seemed inadvisable to attempt to determine the orientation of the nitride plates *in situ*, individual plates were removed by dissolution of the matrix in nitric acid (1:1) after preliminary immersion in aqua regia. Separate large grains of the alpha matrix were prepared by nitrating under controlled conditions, and freed mechanically from grain boundaries and grain-boundary layers. Upon dissolution each of these matrix crystals furnished a large crop of nitride plates, which were washed by decantation with water and alcohol. Fig. 5 shows one of the nitride plates separated from the matrix; this plate was one of those used for the determination of orientation. Fig. 6 shows a plate rather drastically attacked by the etching agent. The largest plates were selected and mounted on a thin celluloid sheet by the use of a dilute alcoholic solution of shellac. It was found possible to obtain and mount well formed plates roughly 1 mm. in diameter. Two alpha matrix crystals were used, the first furnishing a crop of plates from which one good nitride plate was selected for X-ray study, and the second furnishing two plates.

Before determining the orientation of the lattice of these plates with respect to the flat plate surface a large number of plates were combined and a powder X-ray photogram prepared, which showed that only the Fe_4N phase was present, uncontaminated by the epsilon or alpha phases.

Each plate mounted on celluloid was placed in the path of and perpendicular to a pinhole X-ray beam produced at 30 kv. from a molybdenum target, and a photogram was obtained on a flat film also perpendicular to the X-ray beam at a distance of 4 cm. from the nitride plate.

These (three) photograms contained both spots and radial streaks. The spots were reflections of the characteristic radiations Mo K_α and K_β .

from the Fe_4N lattice; the radial streaks were typical asterism streaks from the white radiation.

From these photograms stereographic projections were prepared, with the proper indices assigned to the sharp spots from the K_α and K_β radia-

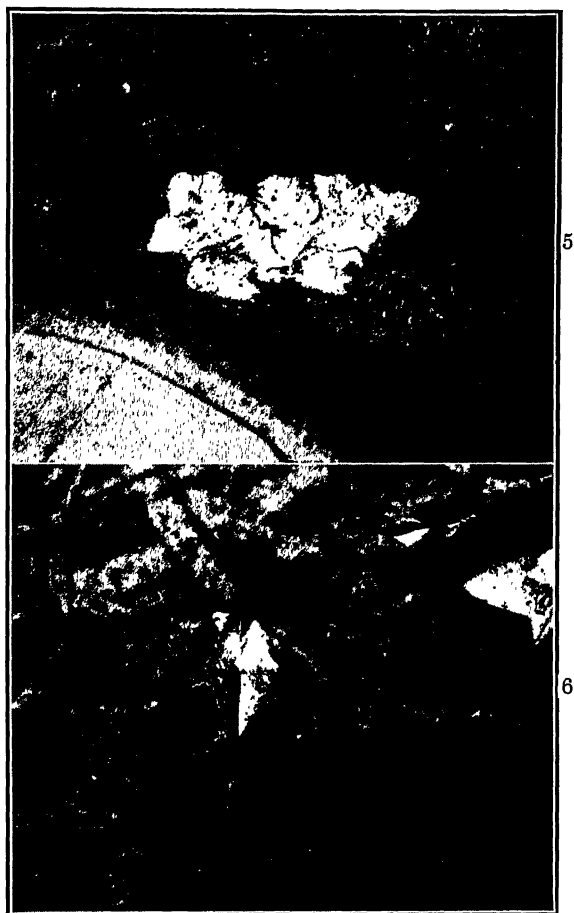


FIG. 5.—SEPARATED NITRIDE PLATE USED FOR X-RAY DETERMINATION OF ORIENTATION. MOUNTED ON CELLULOID. $\times 150$.

Obtained by dissolution of matrix in nitric acid.

FIG. 6.—SEPARATED NITRIDE PLATE DRASTICALLY ETCHED, ON BACKGROUND OF PAPER. $\times 150$.

tion by calculation of the diffraction angles. It was not always possible to determine the index uniquely, but in no case were more than two indices possible and subsequent analysis showed clearly the correct one of the two. These photograms were not sufficiently sharp for reproduction, so only the calculated projections are reproduced here (Figs. 7 and 8).

The Laue streaks likewise were assigned indices: a standard stereographic projection which represented an important reflecting plane of the Fe_4N lattice. The presence of these Laue streaks was proof that a range of orientations occurred in each plate, the approximate limits of which were determined by the following procedure. A rotation was chosen that would bring the points of a standard projection into the vicinity of the corresponding points from the film. The points from the standard projection are represented in Figs. 7 and 8 as open circles and those from the film as full circles, while loci of the planes causing the Laue streaks are represented by heavy lines. The plane of projection in Figs. 7 and 8 is in each case the surface of the nitride plate, so that the normal to the plate (the pole of the plate) lies in the center of the projection, indicated

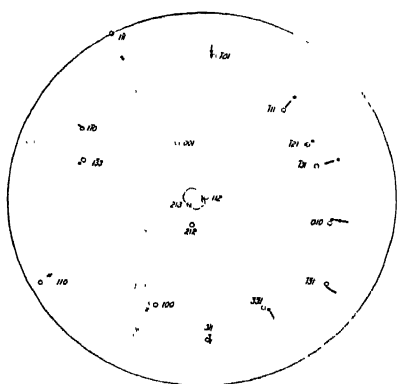


FIG. 7.

FIG. 7.—STEREOGRAPHIC REPRESENTATION OF ORIENTATION OF NITRIDE PLATE. FIRST DETERMINATION.

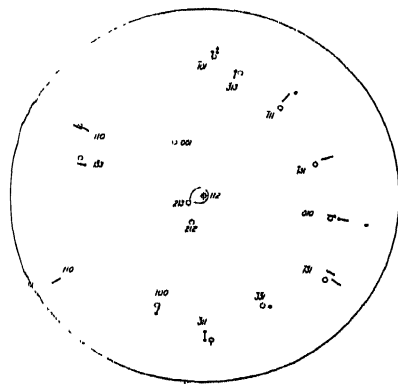


FIG. 8.

FIG. 8.—STEREOGRAPHIC REPRESENTATION OF ORIENTATION OF NITRIDE PLATE. SECOND DETERMINATION.

by the cross. By the use of a rotation net the amount of rotation that would bring each of the heavy lines in turn into coincidence with the corresponding white circles was determined; the rotation was measured in each case about an axis in the projection plane, the plane of the plate, and located at right angles to the radius from the center of the projection to the point in question. The pole of the plate was then rotated the same amount about each of these axes in turn and the area swept out by the pole of the plate was outlined by a smooth curve, shown in the center of each figure. This area represents the orientations of the normal to the plate when the lattice in each part of the plate is in turn brought into line with the standard orientation indicated by the open circles.

This scattering amounts to 5° to 10° and makes the choice of the index of the plane parallel to the plate surface in some respects uncertain. Of the low index planes, only the (112) and (213) are possible solutions; the

choice between these two cannot be made from the figures, but inspection shows that the $\{213\}$ planes in Fe_4N are in no way similar to the $\{210\}$ planes in the alpha phase, either when the atoms on the unit rectangles are considered or when these and the disposition of the atoms on the adjacent parallel planes are considered, while there is a very extensive

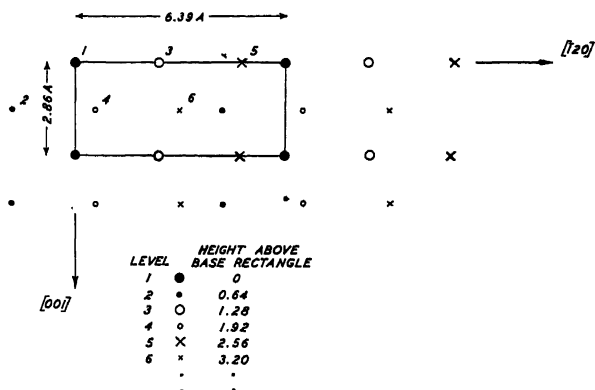


FIG. 9.—PLOT OF ATOMS ON $(210)_{\alpha\text{Fe}}$ PLANE.

similarity in both respects between the $\{112\}$ planes in the Fe_4N phase and the $\{210\}$ planes in the alpha phase, as will be shown (Figs. 9 and 10). Upon this basis the plane in the Fe_4N lattice parallel to the plane of the Fe_4N plate is selected as the $\{112\}$ plane.

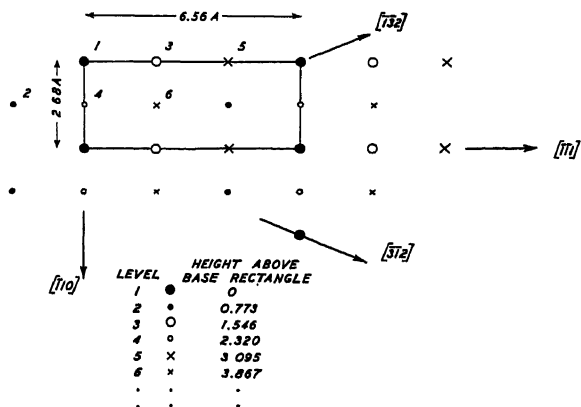


FIG. 10.—PLOT OF ATOMS ON $(112)_{\text{Fe}_4\text{N}}$ PLANE.

The lack of exact coincidence of the surface of the plate with the $\{112\}$ plane in Fe_4N lattice may be ascribed to an inaccurate alignment of the plate perpendicular to the X-ray beam (a difficult feat with such small plates) and the range of orientations perhaps to a fragmentation of the plate during the setting of the shellac cement. No evidence for a

tion observed for the somewhat analogous case in Fe-C alloys,¹¹ is not listed because it shows a much greater difference in dimensions. The combination $\{210\}_{\alpha \text{ Fe}}: \{321\}_{\text{Fe}_4\text{N}}$, suggested in Figs. 7 and 8, is not listed because of complete absence of any similarity.

The lack of convincing reasons in Table 1 for the selection of the observed combination of $\{210\}_{\alpha}: \{112\}_{\text{Fe}_4\text{N}}$ strongly suggests that the simple theory previously enunciated in this series of papers, based entirely upon near identities in atom pattern and in interatomic distances upon single members of the conjugate planes, is not adequate. In an attempt to extend this theory to a matching of atom positions in three dimensions, a series of plots of atom positions on various atom levels was prepared for the combinations listed in the table. Figs. 9 and 10 represent such plots for the planes $(210)_{\alpha \text{ Fe}}$ and $(112)_{\text{Fe}_4\text{N}}$. The plots were made by the method previously described.¹²

The similarity in atom spacing and pattern of these two planes is easily evident in the figures. From the calculated coordinates of the atoms the amount of movement of the atoms in $\alpha \text{ Fe}$ (Fig. 9) in assuming the positions in Fe_4N (Fig. 10) was calculated for the four atoms in each unit rectangle on each level, with the atoms at the origin on the first level initially placed in coincidence.

Similar plots for the other combinations of planes in Table 1 showed that the amount of atom displacement increased much more rapidly with ascending level than for the combination $\{210\}_{\alpha \text{ Fe}}: \{112\}_{\text{Fe}_4\text{N}}$. In other words, this combination shows the best three-dimensional match of the possible combinations that show similar patterns upon the base rectangle. It has always seemed necessary that near approximation to registry in three dimensions should be a part of a theory to explain such crystallographic movements, and this case seems to furnish proof of the importance of this factor. How far such considerations may be extended to other systems cannot as yet be said.

The outward form of the separated nitride plate shown in Fig. 6 bears an interesting relationship to the geometry of the $(112)_{\text{Fe}_4\text{N}}$ plane. The acute angle between the sides of this nitride plate is between 43° and 48° ; and each side accordingly will exhibit an angle of approximately 23° with the long center rib, and 67° with the short center rib. These angles and the right angles formed by the center rib are strongly suggestive of the angles formed by the close-packed directions on the $(112)_{\text{Fe}_4\text{N}}$ plane as shown in Fig. 10: the directions $[\bar{1}10]$ and $[\bar{1}\bar{1}1]$ intersect at right angles, and the $[\bar{1}\bar{3}2]$ direction forms an angle of 22.2° with the $[\bar{1}\bar{1}1]$ direction, as does the direction $[3\bar{1}2]$. These are the closest packed directions

¹¹ R. F. Mehl, C. S. Barrett and D. W. Smith: Studies upon the Widmanstätten Structure, IV—The Iron-carbon Alloys. *Trans. A.I.M.E.* (1933) **105**, 215-249.

¹² R. F. Mehl, C. S. Barrett and D. W. Smith: Reference of footnote 11, Appendix B.

in the $(112)_{\text{Fe}_3\text{N}}$ plane, and the retention of these as crystal edges would not be surprising. The outward form of these etched plates thus may be taken as indirect confirmation of the X-ray determination of the $(112)_{\text{Fe}_3\text{N}}$ plane as the plane lying in the surface of the nitride plate.

PRECIPITATION OF Fe_3P FROM THE SOLID SOLUTION OF P IN ALPHA FE

Constitution of the System Iron-phosphorus

It has been shown by J. L. Haughton¹³ that α Fe dissolves a maximum of 2.8 per cent in solid solution at the eutectic temperature 1050°C .; that this solubility decreases rapidly to 1.0 per cent at 700° , remaining apparently constant at this value to lower temperatures; that the γ Fe field is limited, "loop forming," extending to approximately 0.5 per cent P; and that the compound Fe_3P is in equilibrium with the alpha (delta) solid solution. These data are in approximate agreement with those obtained by Vogel.¹⁴

Crystal Structure of Participating Phases

The lattice parameter of the alpha solid solution is not appreciably altered by phosphorus.¹⁵ The crystal structure of the precipitate, Fe_3P , has not been completely solved, though Hägg has shown that it is body-centered tetragonal, probably belonging to the space group S_4^2 . The axial lengths are $a_0 = 9.090$, $c_0 = 4.446$; the number of atoms in a unit cell is probably 32, but since the parameters have not been determined the positions of the atoms are unknown.

Formation and Outward Form of Precipitate

All of the work reported here was done on an alloy containing 3.2 per cent P, prepared by melting Armco ingot iron in an induction furnace and adding ferrophosphorus, containing 19.67 per cent P, 1.08 per cent Mn, 0.39 per cent Si, 0.034 per cent S, 78.81 per cent Fe, to form an alloy saturated with P in solid solution at the eutectic temperature. The melt was slowly frozen and cooled in the furnace in order to obtain with the minimum effort a large-grained sample with a well defined Widmanstätten figure; the resultant ingot weighed 180 grams. This technique produced amply large grains, some over $\frac{1}{2}$ cm. in diameter, with a well formed structure. The appearance of the structure obtained is shown in Figs. 11 and 12, a structure similar to those observed by Haughton, by Vogel, and by Köster.¹⁶ The phosphide Fe_3P takes the

¹³ J. L. Haughton: Alloys of Iron Research, VIII—The Constitution of Alloys of Iron and Phosphorus. *Jnl. Iron and Steel Inst.* (1927) **115**, 417–442.

¹⁴ R. Vogel: The System Iron-Phosphorus-Carbon. *Archiv Eisenhüttenwesen* (1929) **3**, 369–81.

¹⁵ G. Hägg: Reference of footnote 9.

¹⁶ W. Köster: The Precipitation Hardness of Iron-Phosphorus Alloys. *Archiv Eisenhüttenwesen* (1931) **4**, 609–611.

form of plates, but the intersection of these plates with the surface of polish reveals a fragmentary lacelike structure (Fig. 12). Despite this it

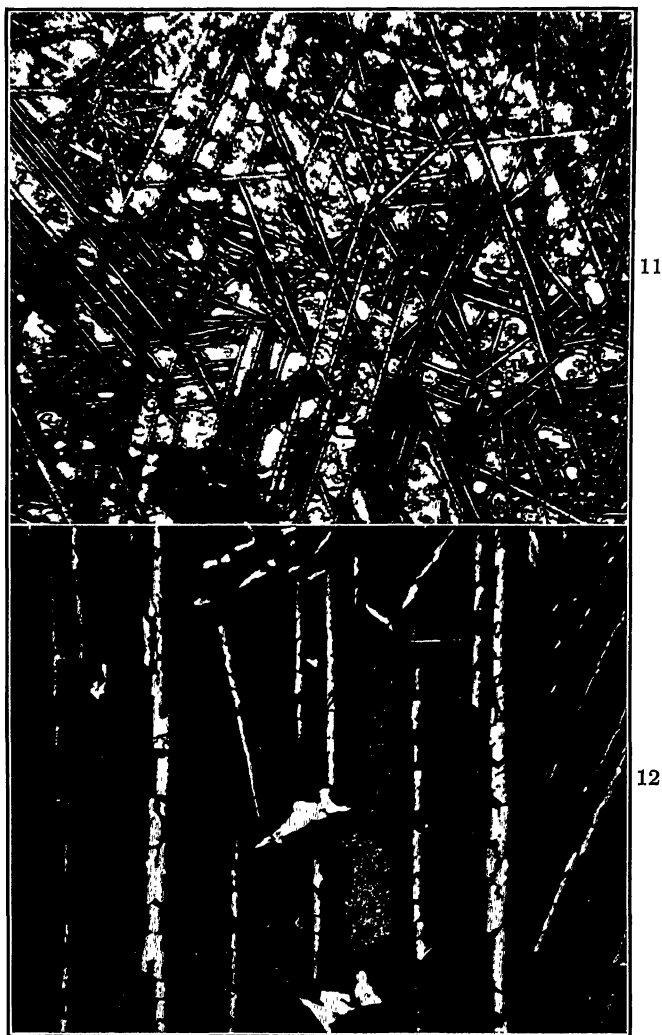


FIG. 11.—WIDMANSTÄTTEN FIGURE IN Fe-P ALLOY CONTAINING 3.2 PER CENT P. $\times 80$.
Etched with Stead's reagent (acid cupric chloride).

FIG. 12.—WIDMANSTÄTTEN FIGURE IN Fe-P ALLOY CONTAINING 3.2 PER CENT P.
 $\times 250$.

Etched with Stead's reagent (acid cupric chloride), followed by light buffing to remove tarnish from phosphide.

proved possible to procure unusually precise measurements of trace direction, as will be seen in the determination of the plane of precipitation.

In order to study this fine structure of the phosphide plate—a structure entirely absent in the nitride plate previously discussed—several phosphide plates were removed from the matrix by cleavage and acid



FIG. 13.—STRUCTURE OF Fe_3P PLATE. MOUNTED ON CELLULOID. $\times 10$
As removed from matrix by dissolution of matrix in nitric acid.

FIG. 14.—STRUCTURE OF Fe_3P PLATE SHOWN IN FIG. 13. $\times 1500$.

dissolution of the matrix. Fig. 13 is a good representation of the lace-like character of the plate. At higher magnification (Fig. 14) the fine structure of the plate is found to be fragmentary in character, the frag-

ments showing varying orientation. Evidently some complication in structure obtains in this Widmanstätten figure.

Determination of Plane of Precipitation

A section of the large ingot was selected and cut so that one large grain, nearly a centimeter in diameter, lay on both sides of an edge, the enclosed angle of which was determined as 88° by a reflection goniometer. The phosphide plate traces in this grain (Fig. 11) were often very long, occasionally over 1 mm., and though only a small percentage of the plates could be traced continuously around the edge, the length and precision of direction of the plates observed permitted rather unusual accuracy in the determination of their direction on one face and in the determination of their position in space by measurement of the angle formed with the edge by single plates on the two surfaces. All measurements were made on photographs taken at 80 dia.; the length of the plate traces measured on these photographs varied between 3 and 100 millimeters.

Frequency curves of directions upon each of the two surfaces were prepared by measurement of the directions of several hundred traces on each surface. The frequency curves obtained, however, apparently showed too many superimposed maxima, and though some of these maxima were sharply marked it proved impossible to determine the plane of precipitation by comparing the location of the trace normals with the poles of the planes of the matrix alpha planes fixed by an X-ray determination, as was done for the Fe_4N plates. The number of maxima was certainly greater than 12, and though 24 maxima could not be determined with certainty, evidently a 24 rather than a 12-family plane was concerned.

In order to determine this 24-family plane uniquely, well formed plates were traced around the edge and their positions in space determined in the usual way. The orientation of the matrix was then determined by X-rays and the observed plate poles and the poles of the planes in the alpha matrix compared upon a stereographic projection.

Fig. 15 is one of the two stereographic projections made; these two represented entirely separate determinations affording identical results of comparable precision. The orientation of the alpha matrix determined by X-rays is represented by the poles, the positions of which were derived directly from the X-ray films—these poles are indicated by crosses; the poles of the phosphide plates are represented by the open circles; the position of the edge of the specimen is represented by the short lines at the left and right of the stereographic circle. The position of the [100] poles may be introduced into this diagram directly from the known angles between these and the poles determined directly by X-rays. Upon rotation of these cube poles into the positions of the standard

projection, with the pole [001] in the center, the poles representing the positions of the phosphide plates take the positions shown by open circles in Fig. 16. These poles were then rotated into one quadrant as shown in Fig. 17 by means of appropriate symmetry operations in order to concentrate the data in an endeavor to assist in an accurate determination of the plane of precipitation.

It will be observed in this figure and in an enlargement of it, Fig. 18, that all 20 points are concentrated in a very limited area. The center of gravity—the average or mean position—of these points corresponds to no plane of simple index. The nearest plane is the $\{12\ 1\ 4\}$ plane, unless a plane of very high index be chosen. A wholly separate determination

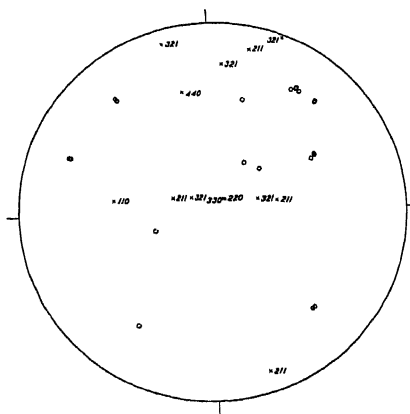


FIG. 15.

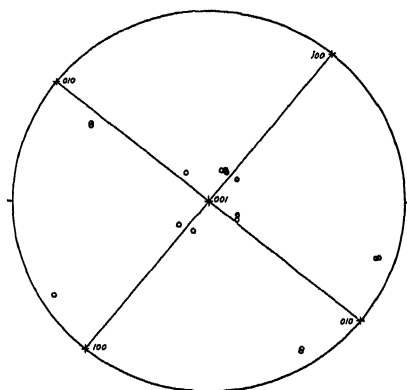


FIG. 16.

FIG. 15.—STEREOGRAPHIC PROJECTION OF POLES OF PHOSPHIDE PLATES.

Crosses represent poles of planes in the alpha matrix as determined by X-rays; circles represent poles of phosphide plates.

FIG. 16.—SHOWING POLES IN FIG. 15 ROTATED INTO A STANDARD PROJECTION.

gave the same result; furthermore, analysis of the plate interpole angles, apart from the data on the orientation of the alpha matrix, led to the same result. The probable errors involved in the determination of the positions of the orientation of the alpha matrix were not sufficiently large to permit a choice of a plane of lower index. The nearest plane of low index, (310), is definitely too far removed.

The identity of the precipitated plates was confirmed by an X-ray powder photogram of some etched-out plates. All diffraction lines agreed with those reported by Hägg for Fe_3P . A determination of the orientation of the lattice in the individual plates was not attempted, although some Laue photograms were taken which indicated an unsymmetrical orientation of the lattice with respect to the surface of the plate. All of the photograms contained evidence of considerable fragmentation of the plates with a deviation sometimes amounting to several degrees between the orientations of the different fragments.

Discussion of Results

The apparent choice of the $\{12\ 1\ 4\}$ planes is unusual, but in view of the incomplete data on the structure of the compound Fe_3P and on the orientation of the Fe_3P with respect to the plane of the plate, no analysis can be attempted. The determination of this plane demonstrates, however, that planes of high index may be chosen, and that no very simple general theory can be advanced to explain these structures. The concentration of the poles of the plates within a very narrow range as shown in Fig. 18 indicates that only one plane in the α lattice is chosen for precipitation, and except for this the fragmentary character of the plate is reminiscent in some respects of the fragmentary character of

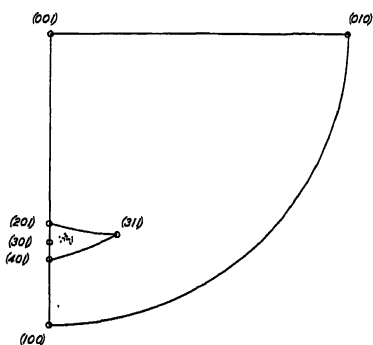


FIG. 17.

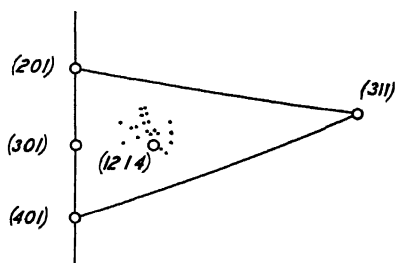


FIG. 18.

FIG. 17.—SHOWING POLES IN FIG. 16 ROTATED INTO ONE QUADRANT OF STEREOGRAPHIC CIRCLE.

FIG. 18.—ENLARGEMENT OF PROJECTION SHOWN IN FIG. 17.

the Fe_3C plate precipitating from austenite.¹⁷ It is not known whether the magnetic transformation in the Fe_3P phase¹⁸ is accompanied by a change in crystal structure; if so, this might help to explain the observed fragmentation. There is no analogy between the Fe_3P and Fe_4N cases, though both form from α Fe solid solutions.

SUMMARY

1. It is shown that the phase Fe_4N precipitating from the solid solution of nitrogen in α Fe takes the form of plates lying parallel to the $\{210\}$ planes in the α Fe matrix. It is further shown that a $\{112\}$ plane in the Fe_4N plane lies parallel to the plane of the plate and thus parallel to a $\{210\}$ plane in the α Fe matrix, presumably with the close-packed strings of atoms in the two planes mutually parallel.

2. Comparison of lattice dimensions shows that no very good reason can be advanced for the selection of these two planes as conjugate planes

¹⁷ R. F. Mehl, C. S. Barrett and D. W. Smith: Reference of footnote 11.

¹⁸ J. L. Haughton: Reference of footnote 13.

in the precipitation process if the matching of atom positions upon single planes alone be considered; other planes show equally or nearly equally good matching. Comparison of atom positions in adjacent atom layers, however, shows that the orientation chosen involves minimum movement during precipitation for several atom layers.

3. It is shown that Fe_3P precipitating from the solid solution of phosphorus in α Fe takes the form of lacelike and fragmentary plates lying approximately parallel to the $\{12\ 1\ 4\}$ planes. The lack of necessary crystal structure data prevented further analysis of this structure.

ACKNOWLEDGMENT

Much of the work reported here was performed at the Naval Research Laboratory, Washington, D. C. The authors wish to express their appreciation to the members of the executive staff of that laboratory for their interest in the work.

DISCUSSION

(F. B. Foley presiding)

L. W. MCKEEHAN,* New Haven, Conn. (written discussion).—This comment has to do with the tentative assignment of indices $(12\ 1\ 4)$ to the planes in α iron on which

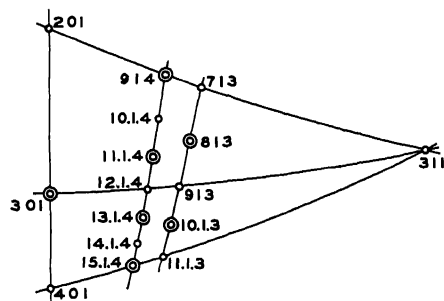


FIG. 19.

Fe_3P plates are found. Fig. 19 shows a large-scale stereographic projection of the triangle shown in Figs. 17 and 18. It will be noticed that there are two planes of lower indices than $(12\ 1\ 4)$ in the near neighborhood—less than 2° away. Of these two, (913) has a higher atomic population in the ratio $\sqrt{161/81} = 1.33$ but lies in the wrong direction. The other, $(11\ 1\ 4)$, has a higher atomic population than $(12\ 1\ 4)$ in the ratio $2\sqrt{161/138} = 2.16$ and seems, as far as can be judged by Fig. 18, to agree

better with the data. The reason for the factor 2 before the last radical is that while $(12\ 1\ 4)$ and (913) have half the normal spacings for a simple cubic lattice, $(11\ 1\ 4)$ has the normal spacing. The other points with double circles are similar to $(11\ 1\ 4)$ in this respect.

R. F. MEHL.—Professor McKeehan's suggestion that the $(11\ 1\ 4)$ plane is more nearly in agreement with the data presented than the $(12\ 1\ 4)$ plane, is true, but the difference is not great. A most probable value for the index of the plane of precipitation in the Fe-P case was not mentioned in the paper, but was obtained by averaging the cosines of the angles between each experimentally located pole and each of the $\{100\}$ poles in turn. For the data presented in Figs. 17 and 18 the average cosines were 0.9397, 0.3319, 0.0785, giving Miller indices very close to $(48\ 17\ 4)$, since the cosines stand in the same ratio as the Miller indices. The angle between $(48\ 17\ 4)$ and $(11\ 1\ 4)$, suggested by Professor McKeehan, is about $\frac{1}{2}^\circ$, while the angle between

* Director, Sloane Physics Laboratory, Yale University.

(48 17 4) and (12 4 1) is about 1° —both obviously within experimental error. The greater atomic population of the (11 1 4) plane, however, is an argument in favor of this plane and we are grateful for the suggestion. I am somewhat inclined to doubt that either of these planes is truly a plane of precipitation in the sense used in this series of papers; that is, a plane parallel to which the precipitate plates lie and parallel to which shearing movements take place, transforming the matrix lattice into the precipitate lattice, for the microstructure of the plates shows a complexity which suggests a complicated mechanism. It is probably wise to withhold the assigning of specific importance to these planes until the Widmanstätten figure is more completely studied.

Observing Formation of Martensite in Certain Alloy Steels at Low Temperatures*

BY O. A. KNIGHT† AND HELMUT MÜLLER-STOCK,‡ STATE COLLEGE, PA.

(New York Meeting, February, 1934)

THE suppression of the austenite-martensite transformation that can be brought about by the addition of certain alloying elements, such as manganese or nickel, to plain carbon steel has been known for a long time, especially since Guillet's investigation at the beginning of this century. The extent to which the critical range is lowered depends upon the percentage and nature of the special element added. First the A_{r1} point is lowered gradually, then at a certain percentage a sudden lowering to about 300° C. occurs. The addition of still larger percentages of the alloy may result in lowering the A_{r1} point to room temperature or below, in which case the steel remains austenitic at room temperature, especially after rapid cooling.

The effect of alloying elements of this general type on the lowering of the transformation temperature is well illustrated by Sauveur⁽¹⁾§ in his Fig. 281a, reproduced here as Fig. 1. This type of curve is characteristic of both manganese and nickel though it requires about $2\frac{1}{2}$ times as much nickel as of manganese to produce the same result. The influence of nickel in retarding the transformation of austenite into the lower transition constituents is due to its lowering of the critical range of the steel, which is also well illustrated by Sauveur⁽¹⁾ (after Osmond) in his Fig. 284, reproduced here as Fig. 2. Scott⁽¹⁵⁾ presents a diagram illustrating the effect of manganese on the A_{c3} and A_{r3} points which is strikingly similar to the diagram above referred to in Fig. 2 concerning the effect of nickel.

Lowering the critical range has the effect of increasing the viscosity, or, rigidity, of the alloy at the time when it is undergoing its transformation, which greatly slows down the transformation reaction velocity, and this, in turn, makes it easier to suppress, wholly or in part, the transformational changes. Reaction rates are normally much slower at low

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§ For references, see bibliography at end of this paper.

temperatures than at higher temperatures due to decrease in atomic mobility with decrease in temperature. It is, therefore, quite easy to obtain austenite at room temperature in certain alloy steels by quenching

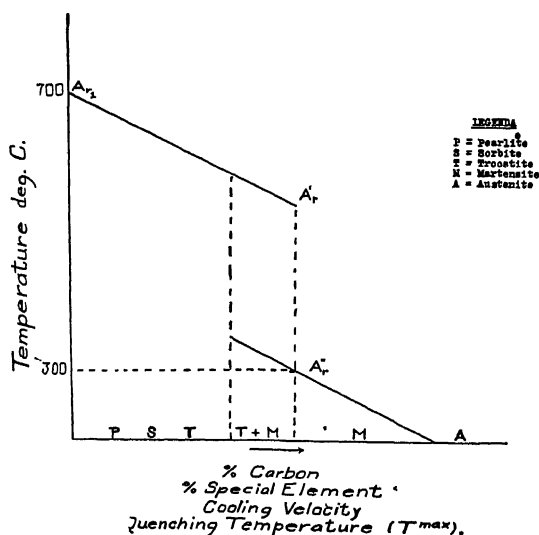


FIG. 1.—EFFECT OF ALLOY ELEMENTS ON TRANSFORMATION TEMPERATURE. (Saweur.)

or even by slower cooling velocities than result from quenching, and some of these steels will transform partly or wholly to martensite when cooled

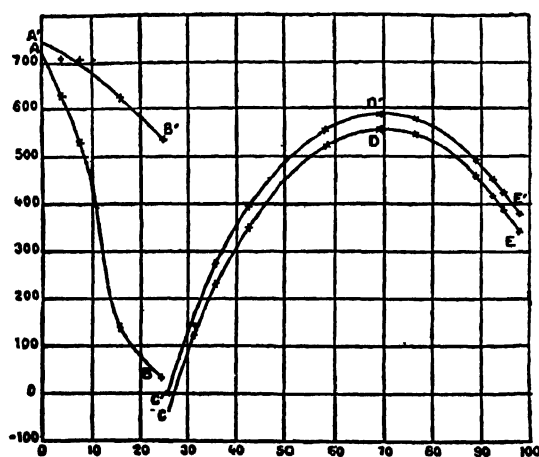


FIG. 2.—INFLUENCE OF NICKEL ON THE CRITICAL POINTS OF IRON. (Osmond.)

to temperatures substantially below room temperature, for instance, by "dry ice" (solid carbon dioxide) mixed with ether, or by liquid air. Hadfield manganese steel is so sluggish in this respect that no noticeable

change in microstructure is observable when it (in the austenitic condition) is cooled to liquid air temperatures. Certain nickel steels, on the other hand, and those containing nickel together with some silicon, are easily made austenitic and retained in that condition at room temperature, but when cooled to sub-zero temperatures transform partially or wholly (apparently) to martensite. The present paper deals with steels that behave in this manner.

PREVIOUS INVESTIGATIONS

The possibility of cold treatment of steel has been known for a considerable time. In 1914 Chevenard⁽²⁾ determined the position of the A_1 point at -125°C . In 1920 Witold Broniewski⁽³⁾ obtained a French patent for "Superficial Hardening of Certain Special Steels" by cooling rapidly to low temperature. Mathews,⁽⁴⁾ Sykes and Jeffries,⁽⁵⁾ Harder and Dowdell,⁽⁶⁾ Honda and Iwasé,⁽⁷⁾ Bain and Waring,⁽⁸⁾ all have worked on the behavior of austenitic steel when treated with liquid oxygen or liquid air. Luerssen and Greene⁽⁹⁾ determined the critical points of some special chromium-nickel and nickel-silicon steels. Tammann and Scheil,⁽¹⁰⁾ and Schroeter,⁽¹¹⁾ ascertained, by means of the change in magnetic properties, that the transformation takes place actually at the low temperature and not after having again reached the room temperature.

The above-mentioned papers have all dealt more or less with the change in physical properties, such as hardness, strength and magnetic permeability, brought about by cold treatment. H. J. Wiester,^(12,13) at the suggestion of Hanemann in Berlin-Charlottenburg, studied the austenite-martensite change in a steel with 1.65 per cent carbon, which can be suppressed to below 100°C ., and he succeeded in taking moving pictures of the transformation. In the United States, Rogers and Van Wert, at Harvard, have also obtained motion picture films of a similar phenomenon (the A_3 transformation in pure iron) but they, too, were working at temperatures well above room temperature.

PRESENT METHODS AND OBSERVATIONS

The object of the present study was to observe under the microscope, if possible, the formation of martensite from austenite at temperatures considerably below room temperature. It was hoped that the reaction velocity would be so slow at these low temperatures that the mechanism of the formation of an individual martensite needle could be closely observed. It was hoped also that these low temperatures could be obtained on the surface of the specimen under observation without injury to the microscope objective. Steels were selected which seemed to be entirely austenitic after brine quenching from 1000°C . but would give

rise to the formation of abundance of martensite when cooled to the temperature of solid carbon dioxide in ether, or of liquid air.

The steels used were furnished by the Carpenter Steel Company, Reading, Pa. They were identical in composition with alloys No. 22 and 24, studied by Luerssen and Greene.⁽⁹⁾ The analyses were as follows:

	C	Mn	Si	P	S	Cr	Ni
A.....	0.16	0.27	3.91	0.011	0.021	0.05	24.97
B.....	0.10	0.24	1.46	0.009	0.026	0.03	25.91

It was believed that etching reagents could be dispensed with, since the volume increase accompanying the formation of martensite produces figures of martensite on a polished surface. Some preliminary work was done to determine whether this were true concerning the steels about to be tested. Several samples were brine-quenched from 1000° C., polished, and then given a bath in liquid air. Subsequent examinations disclosed satisfactory martensite markings on the polished surface. Dry ice and ether gave less impressive results than liquid air. All of these preliminary results were sufficiently encouraging to justify the building of an apparatus which would permit observation of the progress of the change under the microscope.

APPARATUS AND PROCEDURE

As often happens, the first apparatus was entirely too complicated, but by eliminating unnecessary parts it eventually became both simple and workable. Fig. 3 shows the equipment as finally used. In the assembled apparatus, the specimen *A* rested in the threaded cap *B* open at the lower end. Into the upper end of this cap was screwed the threaded pipe *C*, until it rested against the specimen. Between the threaded pipe and the specimen, and between the specimen and the threaded cap, rubber gaskets *I* were inserted to prevent leakage. Tripod *E*, with adjustable feet for leveling, was slipped over the upper end of the threaded pipe and prevented from coming off by the threaded ring *D*. This assemblage could be placed on the microscope stage for examination of the polished (lower) face of specimen, leaving an open space between the threaded cap and the objective *J*, thus making it possible to connect the cap and the objective with a thin rubber hose *K*, into one side of which was inserted the glass bulb *G*, containing phosphorous pentoxide as a desiccating agent. For examination, a brine-quenched, polished specimen was inserted in the apparatus, fresh P_2O_5 was put into the glass bulb, and the assembly was placed on the stage of a large metallograph. The surface of the specimen was leveled and focused, after which several hours were permitted to elapse in order to permit the atmosphere enclosed between the specimen and objective to become thoroughly dry. If this precaution were neglected, moisture would condense and freeze on the specimen and obscure the vision of the metal surface. When

temperature measurements were desired, a very small (28-gage wire), carefully calibrated, copper-constantan thermocouple was employed, with its junction secured to the polished surface of the specimen by a tiny strip of adhesive tape. The image of the specimen was projected

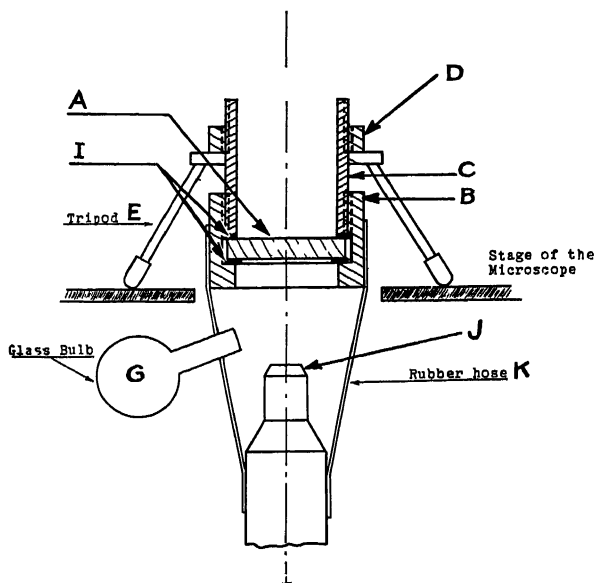


FIG. 3.—APPARATUS FOR OBSERVING EFFECT OF LOW TEMPERATURE ON A METAL SPECIMEN.

on to the ground glass of the metallograph or on to a screen immediately back of the open bellows.

An electric fan was so placed as to prevent the fumes from the liquid air from interfering with the light from the arc. When all was ready, the cooling was done by either solid carbon dioxide and ether or by liquid air. When the former was employed, ether was poured into the container (the bottom of which was the specimen and the sides the threaded pipe) to a depth of about $\frac{1}{2}$ in. and into this, chips of dry ice were inserted. With a little practice, the rate of cooling could be fairly well controlled. The cooling efficiency of the apparatus may be estimated by noting that the thermocouple on the polished surface registered -76° C. when dry ice and ether were used, and well below -150° C. when liquid air was employed. The rate of cooling with liquid air was also susceptible to a certain measure of control by the rate at which liquid air was poured in.

During cooling, the surface of the specimen was constantly watched. Usually nothing happened until a temperature of about -35° C. was reached when, very suddenly, a needle of martensite would appear. Others would follow at various points in the field of observation. The rate at which the needles multiplied seemed to be roughly proportional

to the rate of cooling to lower temperatures. It was observed that each individual needle formed almost instantly to its full size and did not grow subsequently, very much like the popping of pop-corn. After observing this phenomenon a number of times, several attempts were made to obtain moving pictures of the change, thus far without success; it prob-

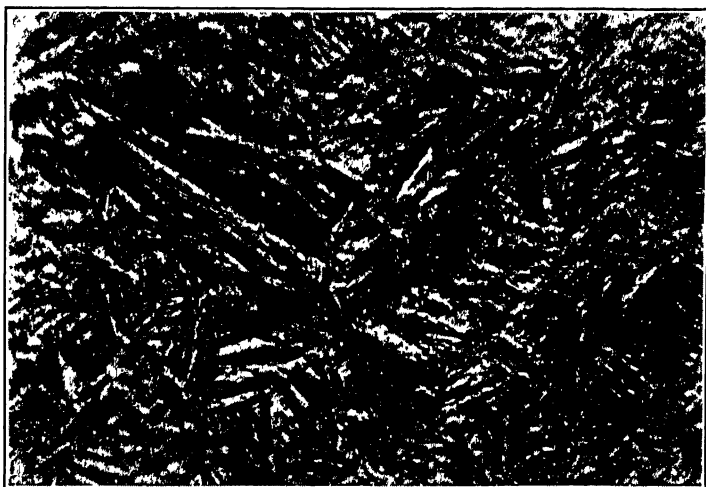


FIG. 4.—STRUCTURE DEVELOPED DURING COLD TREATMENT UNDER THE MICROSCOPE. STEEL A, UNETCHED. $\times 150$.

ably can be done, however, and our efforts are being continued. It is hoped that high-speed pictures can be obtained, which, when projected at "slow motion" will permit the positive determination of the rate of formation of individual martensite needles.

In several instances, one of us happened to be looking directly at the spot on the field when a large martensite needle formed. One end of this needle seemed to appear first, and the rest propagated along the surface to the other end of the full grown needle, like the raising of a ridge by a mole at work, only very much faster. If the formation of an individual needle is slow enough to be actually observable by eye, as seemed to be the case, moving pictures ought to determine the rate accurately. Moreover, the reaction rate at -35° to -150° C. should, theoretically, be so much slower than at $+100^{\circ}$ C. and higher, as to make it capable of determination at the lower temperatures, in view of the results achieved at higher temperatures by Hanemann and Wiester.^(12,13) Hence, although other investigators report that martensite needles form "instantly," it is believed that the speed of formation is such, at the low temperatures of the transformation, as to offer an unusual opportunity for study.

An idea of what was seen to occur during the formation of martensite may be obtained from Fig. 4, which is a photomicrograph of steel A,

after brine quenching from 1000° C., polishing, and treating with liquid air on the microscope. Before the cold treatment, nothing was visible except a plane polished surface. During the cold treatment, the structure shown in Fig. 4 developed. The microstructures of this steel after various mechanical, hot, and cold treatments, as revealed by the usual polishing and etching, is so clearly shown in the paper by Luerssen and Greene⁽⁹⁾ that it was thought unnecessary to repeat them here.

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DISCUSSION

(H. M. Boylston presiding)

H. S. RAWDON,* Washington, D. C. (written discussion).—The method described by the authors is one that is capable of furnishing some very instructive results and useful information on the mechanism of martensite formation in steels. A suitable recording, preferably in the form of motion pictures, is very desirable and essential for studying the surface changes so aptly described by the authors as comparable to the "popping of corn" and the "growth" of a single martensite needle, which as

* Chief, Division of Metallurgy, U. S. Bureau of Standards.

seen on the surface is similar to what one sees as a mole is at work in the ground. In this connection it would seem desirable to experiment with an initially polished and etched surface in order to show whether or not any particular feature in the visible microstructure can serve as a nucleus at which a needle can form and grow.

The characteristic ascicular or needlelike structure of a martensitic steel is without doubt intimately associated with the highly stressed condition of martensitic steel, if, indeed, it is not wholly the result of such a stressed condition, the volume increase resulting from the lattice change being largely the origin of stress. The authors' description of the growth of a martensite needle is very suggestive of what one may see on a larger scale in the formation of the so-called "Luders' lines" in soft steel under stress. In a properly prepared specimen when stressed, one may often trace the progress of the deformation "wave" throughout the body of the specimen. Not infrequently the advancing front of this wave takes the form, as seen from the surface, of a thin sharp needle which slowly penetrates into the as yet undeformed metal.¹⁶ Needles from different origins and proceeding in different directions may intersect and cross each other without losing their identity.

Another feature that lends support to the hypothesis that the martensite "needle structure" is largely a stress phenomenon is the existence of the microscopic cracks in severely quenched steel, which was demonstrated a number of years ago by work carried out by Samuel Epstein and the writer¹⁷ and which has been so beautifully confirmed and extended since by Lucas.¹⁸

So far as the formation and extent of these microscopic cracks are concerned with respect to the structure of the steel, the needles are structural units existing apparently independently of any finger grain structure in the steel.

The writer sincerely hopes that the authors will find opportunity to carry their studies further and be successful in their endeavor to obtain a motion picture showing the details of this phase of the process of martensite formation.

G. V. LVERSEN AND O. V. GREENE,* Reading, Pa. (written discussion).—The difficulties in devising a suitable apparatus for work of this character, and the ingenuity displayed in overcoming these difficulties can only be appreciated by those who have attempted similar metallographic work, and the authors are to be congratulated upon having devised a successful tool to show the formation of martensite in progress.

We should like to ask whether the authors have made any observations on specimens in which the austenite grain boundaries were first developed by etching, and if so in what part of the grain the first martensite appeared; that is, close to the boundaries or close to the center of the grain. Also, whether or not hardness determinations were made before or after passing through the martensite change upon the specimen shown in Fig. 4.

O. A. KNIGHT (written discussion).—The work suggested by Mr. Rawdon, of taking moving pictures of polished and etched structures, was under way at the time this paper was read and has recently (May 21, 1934) been carried out. The results

¹⁶ H. S. Rawdon: Strain Markings in Mild Steel under Tension. R. P. No. 15. U. S. Bur. Stds. *Jnl. of Research* (1928) 1, 467.

¹⁷ H. S. Rawdon and S. Epstein: The Structure of Martensitic Carbon Steels and the Changes in Microstructure which Occur upon Tempering. U. S. Bur. Stds. *Sci. Papers* (1922) 13, 373.

¹⁸ F. F. Lucas: On the Art of Metallography (Howe Memorial Lecture). *Trans. A.I.M.E.* (1931) 95, 4.

* Carpenter Steel Co.

will be described in another paper. Much, however, is yet to be learned by this method of study and it is being continued.

In reply to the questions by Mr. Luerssen and Mr. Greene, it is hoped that work now in progress will definitely show where martensite needles first form within an austenite grain. It is believed that careful study of the moving pictures, properly slowed down, will furnish the answer, but as yet this phase of the work has not been completed. Hardness tests were not made in this preliminary study but in more recent work hardness determinations were made before and after cold treatment as well as after tempering to different temperatures subsequent to cold treating. It is planned to include all these results in a future paper.

Classification of Alpha Iron-nitrogen and Alpha Iron-carbon as Age-hardening Alloys*

BY JOHN L. BURNS, BETHLEHEM, PA.

(New York Meeting, February, 1934)

THE object of this chapter is to present data concerning the effect of the introduction of relatively slight amounts of carbon and nitrogen into supersaturated solution in iron. The study is confined to the alpha temperature range of both the Fe-C and Fe-N systems. The age-hardening characteristics of these two systems are considered. These data are compared to those of other age-hardening alloy systems and a "classification" is essayed.

A.—RELATION OF LATTICE PARAMETER AND ELECTRICAL CONDUCTIVITY TO CHANGES IN PHYSICAL PROPERTIES DUE TO AGING OF FE-C ALLOYS

Since Whiteley¹ in 1927 showed that some of the iron carbide that is normally present in slowly cooled low carbon-iron alloys disappears on rapid cooling from just below the A_1 point, interest has been manifested in the possibilities of age-hardening in these alloys.

Masing and Koch,² and at the same time and independently, W. Koster,³ proved these alloys to be age-hardenable. A. A. Bates⁴ a little later also published an interesting paper on changes in physical properties due to the aging of low-carbon steels. Many other papers have appeared showing changes in physical properties in specific instances due to this same phenomenon.

Manuscript received at the office of the Institute.

* The work presented constitutes a part of the author's thesis as partial fulfilment of the requirements for the degree of Doctor of Science at Harvard University.

¹ Whiteley: *Jnl. Iron and Steel Inst.* (1927).

² Masing and Koch: *Wiss. Ver. d. Siemens-Konzern* (1927) 6, 202-210; *Archiv f. d. Eisenhüttenwesen* (1928-29) 2, 185-186.

³ Koster: *Archiv f. d. Eisenhüttenwesen* (1928-29) 2, 194-195, 503-522.

⁴ Bates: *Amer. Soc. Steel. Treat. Preprint* (1932).

From the changes in physical properties Masing and Koch⁵ likened this aging to that found in duralumin. Dr. Bates believed the hardening to be due to the precipitation of iron carbide. See Fig. 1.

Since that time, however, Fraenkel,⁶ Dr. Merica,⁷ and others have indicated that all age-hardenable alloys do not behave as does duralumin. Duralumin age-hardens at room temperature without any indication of a relief of supersaturation in that the lattice parameter does not change and the electrical conductivity decreases. Aging duralumin at higher temperatures (150° to 250° C.) shows actual relief of supersaturation

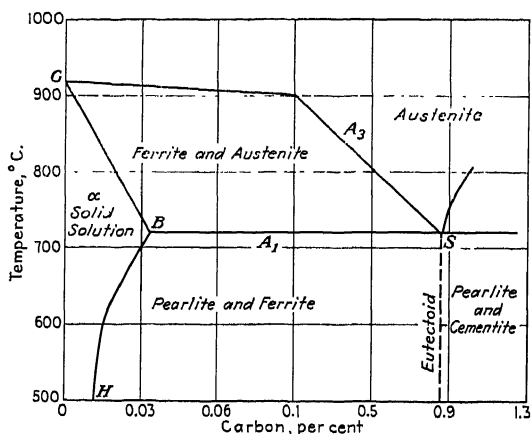


FIG. 1.—CONSTITUTIONAL DIAGRAM IRON-CARBON SOLID-SOLUTION PORTION ENLARGED BY A. A. BATES (*Reprint Amer. Soc. Steel Treat.*, 1931). Point H is disputed, estimations varying from 0.00 to 0.02.

where the parameter approaches that of the solvent and the electrical conductivity increases. There is a hardness increase in both instances.

These facts are the basis of Merica's "knot" theory. This theory proposes as an explanation for the room-temperature hardening that the copper atoms move to segregated spots which he designates as "knots," which make themselves evident by decreased conductivity, increased hardness, and no change in lattice parameter.

He distinguishes this action from the aging at higher temperature, where, he believes, actual precipitation does occur, as shown by the corresponding increase in conductivity and the expected lattice changes. Hardening here is due to the fineness of division of the precipitate.

After reading Dr. Merica's comprehensive survey of the field of age-hardening, one may well feel that to say that an alloy is age-hardenable is a broad statement which may be applied to any alloy that hardens on

⁵ Masing and Koch: Reference of footnote 2.

⁶ Fraenkel: *Ztsch. f. Metallkunde* (1930) **22**, 84.

⁷ Merica: *Trans. A.I.M.E.* (1932) **99**, 13.

aging, but to say that an alloy shows the "duralumin type" of aging definitely classifies it.

For ease of reference, the writer has tried to classify in Table 1 the types of systems one may expect from an age-hardenable alloy based upon the work of others, which are considered in Dr. Merica's paper. From this table one may easily find where his alloy compares, provided he has made the necessary measurements.

Aside from the usual changes in physical property, the other observations necessary in classifying an alloy are the lattice parameter, the electrical conductivity and metallographic examination. Density and slight dimensional changes measured by means of a dilatometer often help.

On the Element Causing Aging in Commercial Steel

In the ordinary commercial steels varying amounts of P, Si, Mn, O, Cu, N and C are found. Of these P, Si, Mn and Cu form solid solutions at room temperature in alpha iron to an extent well beyond the amounts found in ordinary steels. The effect of the presence of these impurities upon the solubility of any one of the group, however, cannot be stated accurately.

Effect of Nitrogen.—The nitrogen present in ordinary steels is lower than that usually reported for the room-temperature solubility. Since the change in solubility of carbon between room temperature and 500° C. is very slight, and since 500° C. is sufficiently high to dissolve all the nitrogen ordinarily present in steel, the effects, if any, may be easily separated. Some preliminary tests indicated that nitrogen need not be considered seriously. The age-hardenable effect, as the previous investigations have shown, is now traceable, principally, to either oxygen or carbon or both.

Effect of Carbon and Oxygen.—An examination of their equilibrium diagrams shows that the maximum solubility of each of these two elements in alpha iron occurs at the same temperature; namely, the A_1 point. This complicates their separation. Attempts have been made to remove the carbon by annealing in hydrogen in order to separate their effects. The difficulties are obvious.

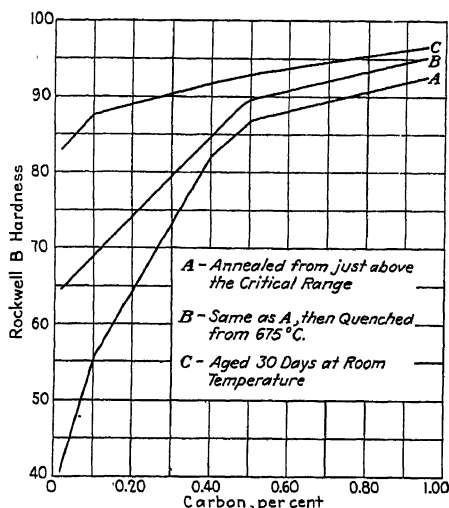


FIG. 2.—EFFECT OF INCREASING CARBON CONTENT ON HARDNESS CHANGES DUE TO AGING OF PLAIN CARBON STEELS.

The change in physical properties of the higher carbon steels on aging are of interest, but they tend to complicate an explanation of the phenom-

TABLE 1.—*Classification of Age-hardenable Alloys*^a

Type	Group	Examples	Electrical Conductivity	Lattice Parameter	Proposed Name
Predicted	A	8 per cent Cu-Ag alloy. Mg-Cu alloys at any age-hardening temp.	Increased	Returns toward solvent lattice	Precipitation-hardening
	B	Cu-Al alloys (duralumin) at 150° to 250° C. At specific temperatures	Increased	Returns toward solvent lattice	Precipitation-hardening
Not Predicted	C	2.5 per cent Be-Cu alloy aging at 200° C. Ti-Ni-Mn steels	Decreased	Returns toward solvent lattice	Precipitation-hardening (?)
	D	Cu-Al (duralumin) alloys aging at room temp.	Decreased	No change	Intrasolution-hardening
	E ^b	Fe-N and Fe-C alloys aging at room temp.	Increased	No change	Intrasolution-hardening

^a Based upon three variables: Temperature, electrical conductivity and lattice parameter. (Hardness increasing in all cases.)

^b From present paper.

TABLE 2.—*Hardness Changes of Carbon Steels*

Carbon, Per Cent	Rockwell B Hardness		
	As Annealed	As Quenched at 675° C.	As Aged 30 Days at Room Temp.
0.02	40.5	64.5	83.0
0.10	55.5	74.5	87.5
0.20	65.0	78.5	88.5
0.40	82.0	85.0	92.0
0.50	87.0	89.5	93.0
0.95	92.5	95.3	96.7

ena. A plot in Fig. 2 of the results in Table 2 brings out the fact that the aging as measured by hardness increase in the higher carbon steels is very slight as compared to that in low-carbon steels. This would tend to

lend credence to the possibility that aging is due to oxygen, and that because the oxygen in solution decreases with increasing carbon content the aging decreases. It should be pointed out, however, that changes in physical properties are not really a measure of precipitation, but an indicator. This is especially true when the original physical properties differ as they do in the case of a low-carbon and high-carbon steel. The X-ray measurements bring this out quite clearly.

Changes in Lattice Parameter of Alpha Iron Due to Quenching from Below the A_1 Point

In this investigation an effort has been made to obtain irons of varying carbon content, but with a sufficiency of oxygen present in each case to meet the maximum solubility requirements in alpha iron. However, according to Zeigler,⁸ the solubility of oxygen increases with decreasing carbon content. The effects should certainly be distinguishable, if this be true.

A Shearer tube (self-rectifying) with a chromium target and a Sachs camera comprised the set-up (Fig. 3). The method of recording used is known as the "back reflection" method. The size of the samples was $\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{4}$ inch.

The solid samples were heated without protection in an electric furnace for $\frac{1}{2}$ hr. at 680° C. and treated as specified. The preparation of a sample for the X-ray measurements consisted in polishing down through 00 paper and etching lightly with a 5 per cent nital solution.

Effect of Carbon.—The results from Table 3 are plotted in Fig. 4. The effect of increasing carbon content upon the lattice parameter of alpha iron is readily discernable. The carbon atom, on being allowed to enter the interstices of the iron lattice at the higher temperature, is retained in its interstitial type of solid solution (supersaturated) by quenching in iced brine. The resulting effect is an enlarged lattice reflected in the increase in dimensions of the cube edge.

Effect of Oxygen.—Since the solubility of the oxygen increases with decreasing carbon, and since the cube edge decreases with decreasing carbon in solution, it seems obvious that oxygen is not the cause for supersaturation. Further proof of the inability of oxygen to cause supersaturation is given by the Wemco iron shown in Fig. 5. This iron was obtained from the Westinghouse Research Laboratories and its analysis, which was supplied by them, is as follows: C, 0.004 per cent; N, 0.004; O, 0.10. Twenty-four other elements were analyzed. Fe by difference = 99.85 per cent (excluding oxygen). No change in lattice parameter is noted on quenching from 680° C., though the total oxygen content is high.

⁸ Zeigler: Amer. Soc. Steel Treat. *Preprint* (1932).

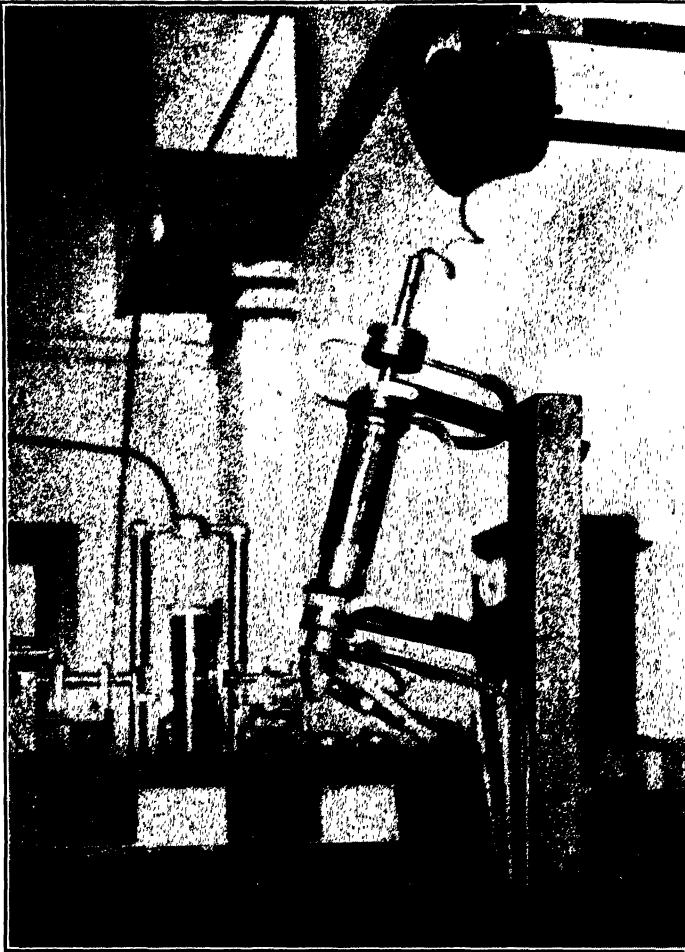


FIG. 3.—X-RAY APPARATUS USED IN THIS INVESTIGATION.

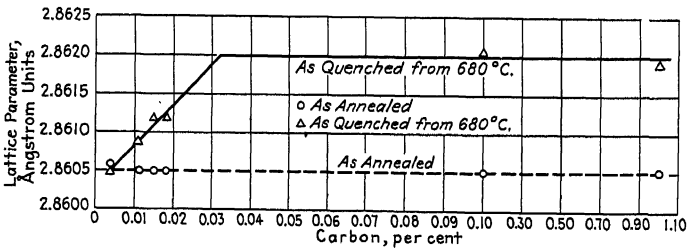


FIG. 4.—EFFECT OF INTRODUCTION OF CARBON IN SOLUTION (SUPERSATURATED) IN ALPHA IRON.

TABLE 3.—*Effect of Increasing Carbon Content on Lattice Parameter of Alpha Iron*

Sample	Total Carbon, Per Cent	As Annealed from 680° C.		As Quenched from 680° C.		Change in Å. Due to Quench
		C in Solution, Per Cent	Å.	C in Solution, Per Cent	Å.	
A	0.004	0.004	2.8606	0.004	2.8605	0.0000
B	0.011	0.005	2.8605	0.011	2.8609	0.0004
C	0.015	0.005	2.8605	0.015	2.8612	0.0007
D	0.018	0.005	2.8605	0.018	2.8612	0.0007
E	Commercial 0.10	0.005	2.8605	0.035	2.8621	0.0016
F	Special 0.10	0.005	2.8604	0.035	2.8619	0.0015
G	0.95	0.005	2.8605	0.035	2.8619	0.0014

Effect of Ordinary Impurities.—In an experiment to determine the effect of ordinary impurities upon the solubility of carbon in alpha iron a commercial 0.10 per cent carbon steel was compared to a specially purified 0.10 per cent carbon steel. The latter was prepared by adding 0.15 per cent carbon to the pure Westinghouse iron described above and melting in vacuo. A comparison of the results may be seen in Table 3.

Fig. 6A is a plot of the results of Table 4. There is no change recorded in lattice parameter during aging at room temperature.

TABLE 4.—*Change in Lattice Parameter With Aging at Room Temperature in 0.10 Per Cent Carbon Steels*

LATTICE PARAMETER IN ÅNGSTRÖMS

Sample	As Annealed	As Quenched at 680° C.	4 Days at Room Temp.	12 Days at Room Temp.	30 Days at Room Temp.
Commercial 0.10 per cent C steel, SAE 1010.....	2.8605	2.8621	2.8621	2.8621	2.8621
Specially purified 0.10 per cent C steel.....	2.8604	2.8619	2.8619	2.8619	2.8619

Hardness and Tensile Strength

Figs. 6E and 6F are plots of the hardness results reported in Table 5, which shows maximum hardness in aging at room temperature. A corroboration of this fact is obtained from the increase in tensile strength under like conditions. It must be remembered, however, that in age-

hardening systems tensile strength and hardness do not always attain their maxima at the same time, although they generally do.⁹

The maximum hardness and strength are recorded by aging at room temperature, whereas no changes occur in the lattice parameter. This

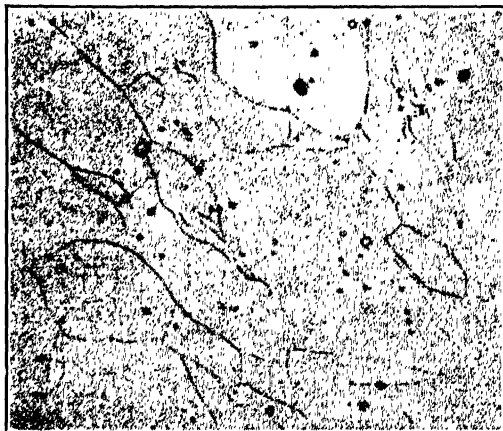


FIG. 5.—IRON-OXIDE INCLUSIONS IN WEMCO IRON. $\times 75$.

fact would seem to indicate that in this system room-temperature hardening is chiefly a function of the atomic motion within the supersaturated solution prior to its true decomposition, as explained by Dr. Merica.

The effect of aging on the tensile strength is shown also in Table 5.

TABLE 5.—*Effect of Aging on Mechanical Hardness and Tensile Strength of SAE 1010 Steel*

ROCKWELL B HARDNESS

As annealed.....	55.5	$\frac{1}{2}$ hr. at 50° C.....	77.2
As quenched at 675° C.....	74.5	$\frac{1}{2}$ hr. at 75° C.....	85.0
10 days at room temperature.....	83.0	$\frac{1}{2}$ hr. at 100° C.....	82.0
30 days at room temperature.....	87.5	$\frac{1}{2}$ hr. at 225° C.....	
100 days at room temperature.....	89.5	$\frac{1}{2}$ hr. at 500° C.....	58.3
		$\frac{1}{2}$ hr. at 700° C.....	55.5

TENSILE PROPERTIES

Treatment	Tensile Strength, Lb. per Sq. In.	R. A., Per Cent	Elongation, Per Cent in 2 In.
As annealed.....	55,600	38.4	32.8
As quenched at 680° C.....	63,500	38.4	30.1
30 days at room temp.....	83,600	32.4	20.5

⁹ Archer and Kempf: *Trans. A.I.M.E.* (1931) **93**, Inst. Metals Div., 114.

Hanson and Ford: *Jnl. Inst. Metals* (1924) **32**, 335.

Changes in Microstructure

The effect of rapid cooling upon the microstructure is best illustrated in a sample in which no pearlite is present. For this purpose, an Armco iron sample containing 0.018 per cent C was used.

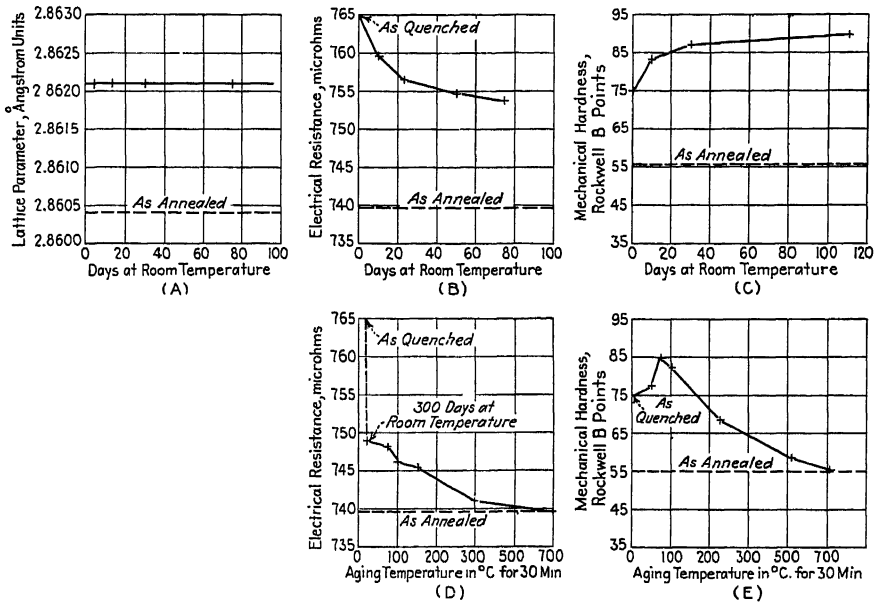


FIG. 6.—HARDNESS, ELECTRICAL CONDUCTIVITY AND LATTICE PARAMETER CHANGES DURING AGING IN A 10 PER CENT CARBON STEEL OF S.A.E. CLASSIFICATION.

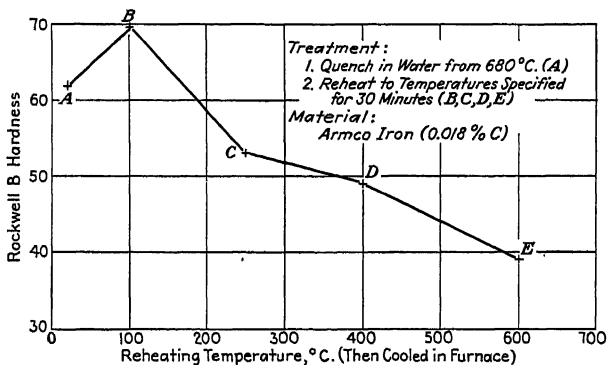
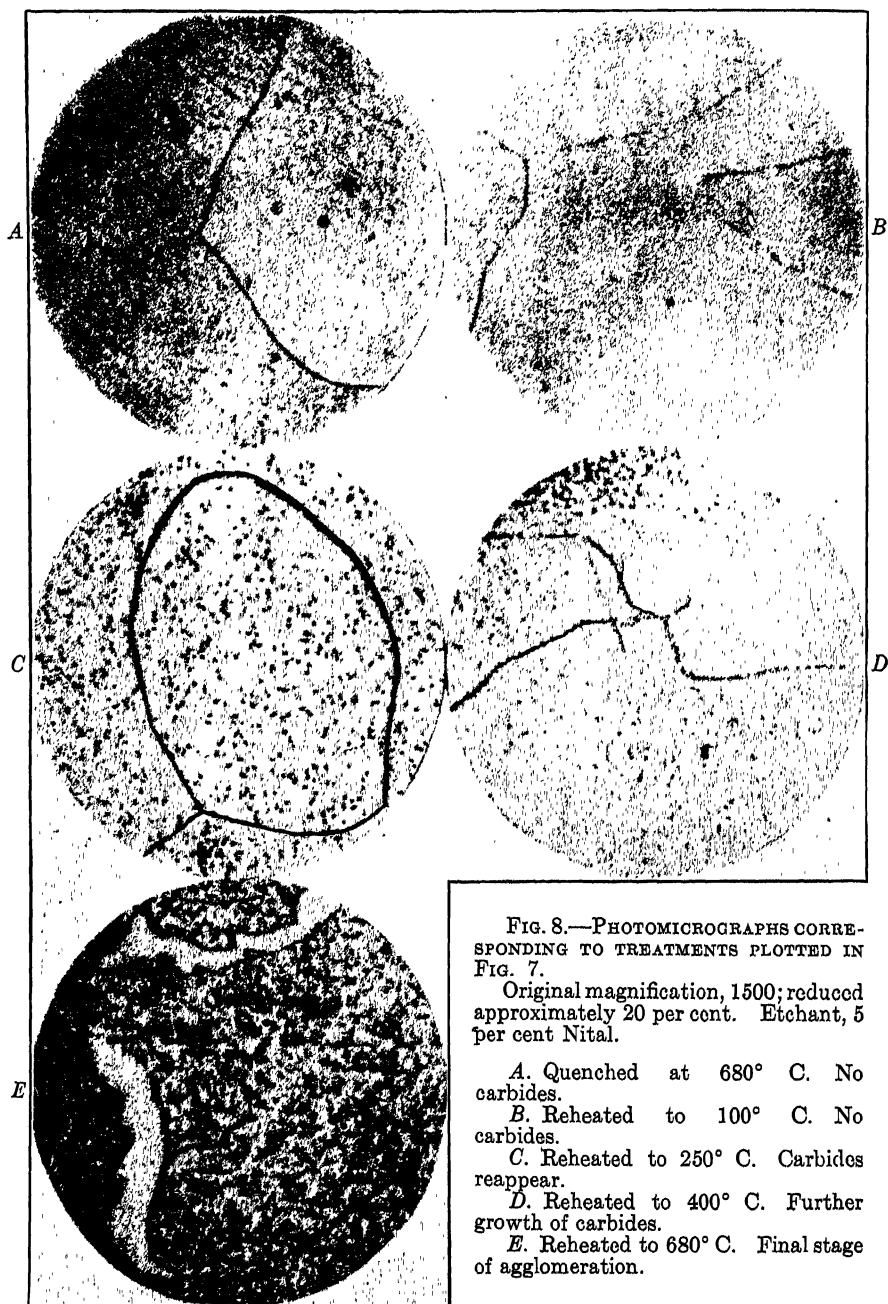


FIG. 7.—EFFECT OF TEMPERATURE UPON THE HARDNESS OF QUENCHED ARMCO IRON. SEE ALSO FIG. 8.

Fig. 7 is a plot of the hardness results and Fig. 8 shows the disappearance and then the appearance of the carbide particles, as the steel is aged at increasingly higher temperatures after quenching.



Electrical Conductivity

A study of the changes in electrical conductivity should throw further light upon the mechanism of age-hardening in this system. A sample of the same 0.10 per cent carbon steel used in the X-ray investigation was drawn down to approximately $\frac{1}{4}$ -in. square rod for conductivity work. The rod was then annealed and polished to remove the scale and the surface decarburizing effect.

Fig. 6B (Table 6) illustrates the decrease in electrical conductivity due to quenching this 0.10 per cent carbon steel from 680° C. It may be seen, then, that the conductivity increases during aging at room temperature, even when no precipitation or relief of supersaturation is indicated by the X-ray measurements.

TABLE 6.—*Changes in Electrical Resistance Due to Aging*
EXPRESSED IN MICROHMS

As annealed.....	739.8	74 days at room temperature....	753.8
As quenched at 680° C.....	765.9	134 days at room temperature....	753.2
3 hr. at room temperature.....	765.9	300 days at room temperature....	749.0
24 hr. at room temperature....	764.8	$\frac{1}{2}$ hr. at 75° C.....	748.0
10 days at room temperature....	759.5	$\frac{1}{2}$ hr. at 100° C.....	746.0
26 days at room temperature....	756.6	$\frac{1}{2}$ hr. at 150° C.....	745.5
51 days at room temperature....	754.7	$\frac{1}{2}$ hr. at 300° C.....	740.5

$$\text{Percentage increase in resistance by quenching} = 100 \frac{765.9 - 739.8}{739.8} = 3.52 \text{ per cent}$$

$$\text{Temperature} = 25.0^\circ \text{ C.} \pm 0.1^\circ \text{ C.}$$

$$\text{Error} = \pm 0.1 \text{ per cent}$$

In other systems a decrease in conductivity is usually noted during aging where "knots" are formed.

Dilatometric Changes

Figs. 9 and 10 exhibit the dilatometric changes due to the aging of the 0.10 per cent carbon steel. This study was made possible by the use of a Chevenard photographic dilatometer.

An annealed 0.10 per cent carbon steel and a 0.10 per cent carbon steel of the same material which had been quenched from 680° C. were used as the "standard" and the "unknown," respectively. These samples were then placed in the dilatometer and heated to 400° C. The result is shown in Fig. 9. A contraction of the quenched sample occurred, which further corroborates the contraction recorded in the X-ray data.

For the sake of comparison, the samples were left untouched and reheated to 400° C. It is obvious that there was no further change in length of the quenched specimen.

Conclusions

The following conclusions were suggested by the foregoing experiments:

1. There is no measurable supersaturation of oxygen produced in alpha iron by quenching from just below the A_1 point, according to X-ray measurements.
2. The lattice parameter of alpha iron is increased with the introduction of carbon in supersaturated solution.

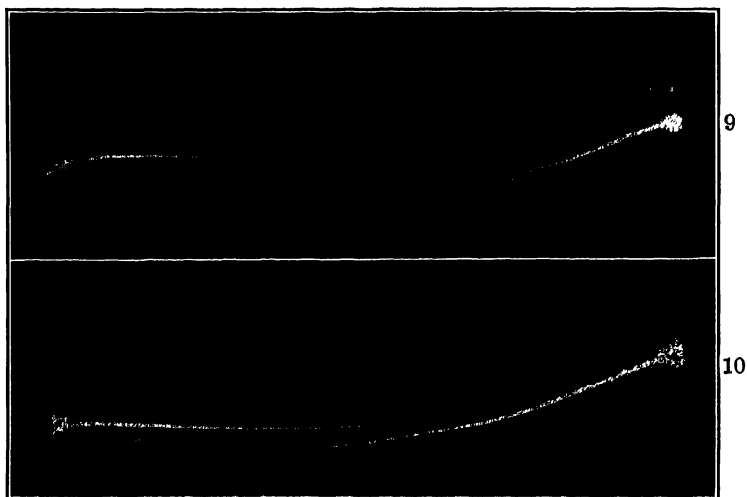


FIG. 9.—SHOWING EXPANSION THAT TAKES PLACE ON AGING A 10 PER CENT CARBON STEEL FOR $\frac{1}{2}$ HOUR AT 400°C . (CHEVENARD PHOTOGRAPHIC DILATOMETER.)

FIG. 10.—SAME MATERIAL AS FIG. 9 REHEATED TO 400°C ., INDICATING THAT NO FURTHER EXPANSION OCCURS.

3. There is no change in lattice parameter on aging at room temperature.
4. The electrical conductivity is decreased by introduction of carbon in supersaturated solution in alpha iron.
5. The electrical conductivity increases on aging at room temperature, and continues to do so on aging at higher temperatures, reverting back toward the annealed reading all the while.
6. The hardening, during the room-temperature aging, apparently is due to some motion within the supersaturated solution before its true decomposition.
7. Manganese and other impurities present in ordinary steel apparently have no measurable effect upon the lattice parameter of iron. The annealed purified iron plus carbon alloy used in this work had the same lattice constant as the annealed commercial steel.
8. The commercial steel showed the same lattice changes due to quenching as did the purified iron-carbon alloy. This would seem to

indicate that the effect of ordinary impurities found in steel upon the solubility of carbon in alpha iron, even with increasing temperature, is very slight.

B.—X-RAY STUDY OF CAUSES OF AGE-HARDENING IN WELD METAL

The fact that both ordinary low-carbon steel and weld metal become embrittled by rapid cooling from below the A_1 point followed by subsequent aging is well known. The chief difference between the weld metal and ordinary steel is the high nitrogen and oxygen content of the former, which is introduced during the welding operation, particularly nitrogen.

Koster^{9a} was the first to note the effect of hardening of nitrogenized iron or steel after quenching and aging. See Fig. 11. Koster and Masing and Koch¹⁰ independently showed that carbon, also, may cause the aging of steel.

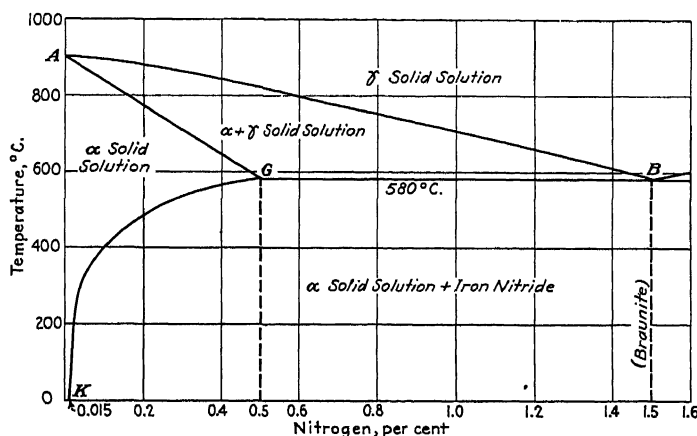


FIG. 11.—CONSTITUTIONAL DIAGRAM OF IRON-NITROGEN ALLOYS BY WERNER KOSTER (*Metals & Alloys*, JUNE, 1930). COMPOUND IS GIVEN AS Fe_4N .

Numerous other papers on the effect of aging upon the physical properties of steel have appeared since that time. The various investigators have also discussed the effect of oxygen upon the aging of steel. This has been a bit difficult to determine.

More recently Hensel and Larsen¹¹ have discussed the effect of aging upon the physical and electrical properties of weld metal. Their paper brought forth a great deal of discussion, especially regarding the cause of the age-hardening. Hensel and Larsen decided that the aging during rest

^{9a} Koster: *Archiv f. d. Eisenhüttenwesen* (1930) **3**, 1553-1558.

¹⁰ Masing and Koch: First reference of footnote 2.

¹¹ Hensel and Larsen: *Trans. Amer. Soc. Steel Treat* (1932) **19**, 639.

at room temperature after quenching from 600° C. was due to a sub-microscopic precipitation of nitrides from the supersaturated solution.

Preparation of Samples

The present paper deals with an artificially prepared "weld" metal. Armco iron containing 0.014 per cent C, 0.004 per cent N, 0.010 per cent Si, 0.015 per cent Mn, 0.025 per cent Cu and 0.015 per cent S was nitrogenized in order to determine the effect of the addition of nitrogen upon the various properties of the metal. Samples of a round ingot-iron bar $\frac{3}{4}$ in. in diameter and 0.2 in. long were nitrided for 111 hr. at 525° C. and slowly cooled in the furnace in the stream of ammonia. The nitrided samples were then placed in cast-iron chips and annealed for 100 hr. at 650° C. to homogenize the nitrogen distribution. That this was accomplished was proved by analyses taken from three different layers from the outside to the center of a sample. The nitrogen content after this treatment was 0.10 per cent.

For the sake of terminology, the nitrogen-bearing iron will be called the "weld" metal, and the iron "as received" the "base" metal.

Effect of Nitrogen upon Lattice Parameter of Alpha Iron

Fig. 12 is a plot of the data in Table 7. These data show clearly the marked increase in lattice parameter caused by quenching the nitrogen-

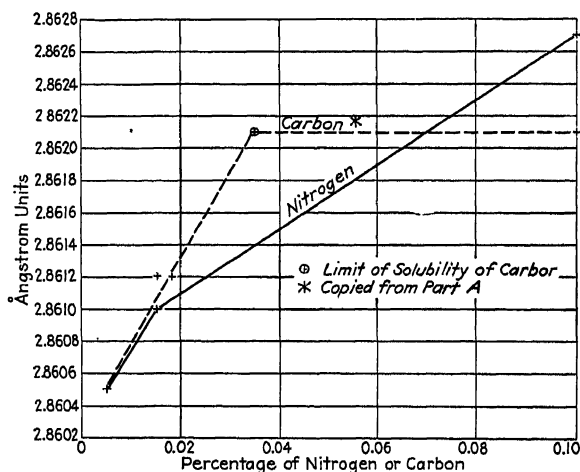


FIG. 12.—EFFECT OF INCREASING NITROGEN AND CARBON UPON LATTICE PARAMETER OF ALPHA IRON.

containing weld metal in iced brine. The annealed weld-metal parameter likewise, but to a lesser degree, is larger than the annealed base-metal parameter. This probably is due also to the difference in nitrogen in solution. The base metal contains only 0.005 per cent nitrogen and since

the room-temperature solubility of nitrogen in alpha iron is usually regarded as 0.015 per cent the "weld" metal will contain 0.010 per cent

TABLE 7.—*Effect of Increasing Nitrogen in Solution in Alpha Iron upon the Lattice Parameter*

Material	Treatment	Percentage of Nitrogen in Solution	Lattice Parameter, A.
Base metal.....	Annealed	0.004	2.8605
Weld metal.....	Annealed	0.015	2.8610
Weld metal.....	Quenched from 510° C. in iced brine	0.10	2.8627

more nitrogen in solution than the "base" metal in the slowly cooled condition.

Interrelated Effect of Carbon and Nitrogen

It is interesting to note that, when carbon and nitrogen are together at a temperature sufficiently high to dissolve both, their effects, after quenching, upon the lattice parameter are not additive. That is to say, when the "weld" metal is quenched from 500° and 650° C. the same lattice reading obtains, but when the base metal is quenched from 500° C. no increase is recorded, whereas a quench from 650° C. does institute an increase in lattice parameter. Since the carbon content is the same in the weld and base metal, does this not mean that when both N and C are present N is dissolved by preference?

A microscopic study was made of this point. When the base metal was quenched from 510° C. in iced brine no noticeable change occurred in the number or size of the carbide particles. But when the base metal was quenched from 650° C. in iced brine the carbides disappeared.

The same two quenching treatments were carried out on the nitrogenized iron or weld metal and the same effects upon the carbide obtained. (No nitride needles were present in either case.)

The only conclusion that can be drawn is that nitrogen does not have a very great effect upon the solubility of carbon in alpha iron.

Another interesting fact about these two atoms, nitrogen and carbon, which form interstitial solid solutions in alpha iron, is the great difference in their solubility limits and yet the similarity of their respective sizes. Nitrogen has a maximum solubility of 0.50 per cent at 580° C., while carbon has only a maximum solubility of 0.03 or 0.04 per cent at 720° C. The radius of the nitrogen atom is given as 0.71 A., according to van Arkel,¹² Becker and Ebert,¹³ and Connell and Mark.¹⁴ The first three

¹² Van Arkel: *Physica* (1924) 4, 286.

¹³ Becker and Ebert: *Ztsch. f. Physik* (1925) 31, 268.

¹⁴ Connell and Mark: *Jnl. Amer. Chem. Soc.* (1925) 47, 281.

named calculated this value from Goldschmidt's¹⁵ work on nitrides of Ti, V, Zr and Nb, all of which crystallize in a sodium chloride type of lattice. The last two investigators calculated this value from the distance between the carbon and nitrogen atoms in hexamethylene-tetramine, which they determined to be 1.48 Å., then assuming carbon to have a radius of 0.77 Å., which is found to be true in the diamond.

It might be well to point out, however, that Ott¹⁶ calculated a value of 0.46 Å. radius for the nitrogen atom, using aluminum nitride and that R. Blix¹⁷ calculated a value of 0.82 Å. from chromium nitride.

Hardness Changes Due to the Introduction of Nitrogen

Fig. 13 indicates that the hardness of the weld metal increases markedly on aging at room temperature without any change in the lattice parameter. This would seem to indicate that the hardening at room temperature is not due to a precipitation of iron nitride, as supposed by

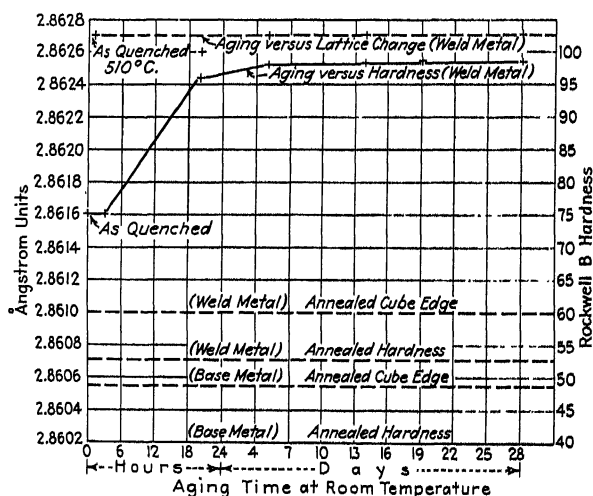


FIG. 13.—EFFECT ON WELD METAL OF AGING AT ROOM TEMPERATURE.

the previous investigators, but an "intrasolution" type of hardening, or, as Dr. Merica¹⁸ would say, a "knot-type" of hardening.

Again, the peculiar difference between duralumin and the Fe-N alloy is that during the knot formation duralumin exhibits a decrease in electrical conductivity while the Fe-N alloy exhibits an increase.¹⁹ This is not peculiar to Fe-N alloys, however, for, as has been shown, the Fe-C

¹⁵ Goldschmidt: *Seochem. Vert. Geschichte* (1926) 7, 27.

¹⁶ Ott: *Ztsch. f. Physik* (1924) 22, 201.

¹⁷ Blix: unpublished data.

¹⁸ Merica: Reference of footnote 7.

¹⁹ Hensel and Larsen: Reference of footnote 11.

alloys behave similarly, both as regards the conductivity increase and the constant lattice parameter, during room-temperature aging.

The 2.5 per cent Be-Cu alloy²⁰ shows a decrease in conductivity, while actual precipitation is occurring at 200° C., but it records a decrease then increase on aging at 250° C. The phenomena presented in this paper are not so surprising when these other results are viewed.

The so-called "incubation period," or rest immediately after quenching, during which no hardening takes place is exhibited by the Fe-N alloy also (Fig. 12). The hardness reading after quenching and after 2 hr. rest (during which the as-quenched X-ray picture was taken) were 75.0 and 75.3 Rockwell B, respectively.

The fact that the two elements, N and C, do not have additive effects when present together, as pointed out in the X-ray results, is corroborated in the hardness findings. Quenching the weld metal from 500° and 650° C. does not show much difference in hardness increase, either as

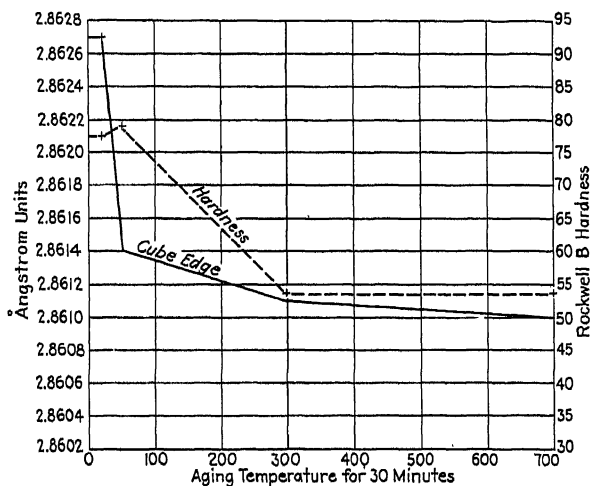


FIG. 14.—EFFECT ON WELD METAL OF AGING AT ELEVATED TEMPERATURE.

quenched or during subsequent aging, whereas quenching the base metal from these temperatures shows marked differences. After quenching from 500° C. the base metal shows very slight hardness increase but after a quench from 650° C. shows a marked increase in hardness.

Conclusions

1. The lattice parameter of alpha iron is increased by the introduction in supersaturated solution of nitrogen in amounts ordinarily found in weld metal.

²⁰ Masing and Dahl: *Wiss. Ver. a. d. Siemens-Konzern*. (1929) 8.

2. This nitrogen is *not* rejected during aging at room temperature, though large hardness increases are reported.

3. There seems to be no additive effect of carbon and nitrogen in supersaturated solution. Both X-ray and hardness results seem to indicate that the nitrogen is not affected by the presence of carbon.

4. Koster and Hensel and Larsen show an increase in conductivity on aging at room temperature. This fact, combined with the X-ray results, likens the Fe-N to the Fe-C system described in section A of this paper.

5. The age-hardening characteristics are not different in the weld metal when quenched from 500° or 650° C. The age-hardening characteristics in the base metal are increased considerably by quenching from 650° C. as compared to 500° C.

6. The normal cube edge of alpha iron containing less than the room-temperature solubility of nitrogen is slightly enlarged by the fulfilling of this solubility as in slowly cooled weld metal.

7. Dr. Merica's knot theory seems to explain the age-hardening phenomena in this system as it does in some other alloy systems, and this despite the fact that the Fe-N alloy shows the conductivity increasing during the knot formation.

8. The characteristic "incubation period" of age-hardening alloys is reported in weld metal also. That is, no hardening takes place during the first few hours of rest at room temperature.

GENERAL DISCUSSION

Table 1 contains a summary of previous investigations of age-hardenable alloys. It shows that duralumin, during aging at room temperature, exhibits decreasing conductivity and no lattice change. It also indicates that duralumin, during aging at elevated temperatures, showed increasing conductivity and a return of the lattice parameter value to that of solvent. The 2.5 per cent Be-Cu alloy showed a decrease in conductivity while the lattice parameter returned toward that of the solvent.

According to the "classical" theory, one should have predicted that during aging the electrical conductivity should increase and that the lattice reading should return toward that of the solvent. If one considers the conductivity increase and return of the lattice constant toward that of the solvent value to be "predicted" behavior, during aging, then from the foregoing there are the following combinations:

Example	Lattice Parameter	Electrical Conductivity
Duralumin at 150° C.	Predicted	Predicted
Duralumin at room temp.	Not predicted	Not predicted
2.5 per cent Be-Cu alloy at 200° C.	Predicted	Not predicted

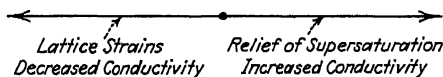
Predicted = *P*

Not predicted = *N*

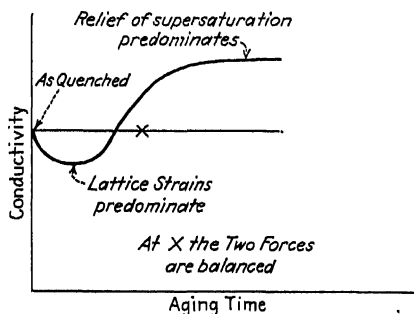
Mathematically, there are four possibilities with respect to lattice parameter and electrical conductivity respectively; namely ($P - P$) as in duralumin at 150° C., ($N - N$) as in duralumin at room temperature, ($P - N$) as in 2.5 per cent Be-Cu alloy at 200° C. and ($N - P$) which we intend to fulfill from the study of the Fe-C and Fe-N systems at room temperature. So to complete the picture:

Example	Lattice Parameter	Electrical Conductivity
Fe-C at room temp. and Fe-N at room temp.	Not predicted	Predicted

This seems to indicate that electrical conductivity changes during aging must be a function of at least two factors. Apparently, either may predominate. Pictured vectorially, this would be



A summation of these effects gives the resultant that we read. If this is true, then theoretically one might obtain the condition where the conductivity does not change during the age-hardening due to a balancing of these two forces. This is actually obtained momentarily when aging some alloys at a temperature where the conductivity decreases, then increases, and in increasing passes the zero point, or graphically:



The fact is also brought out that conductivity may be increased or decreased during knot formation as well as during true precipitation. Conductivity, therefore, cannot be used in itself as an indicator of knot formation or of true precipitation.

ACKNOWLEDGMENTS

This investigation was carried out under Dr. Albert Sauveur, Gordon Mackay Professor of Metallurgy at Harvard University. The author

wishes to express his deepest appreciation to Professor Sauveur for his constant interest and encouragement. He has drawn freely from Professor Sauveur's many suggestions.

Prof. John T. Norton and Dr. L. C. Hicks of Massachusetts Institute of Technology allowed the writer to carry on his X-ray investigations in their laboratory. The camera was built by Dr. Hicks. Professor Norton's suggestions in the X-ray investigation and the general subject were very helpful to the writer.

Dr. J. B. Clough is responsible for the preparation and analyses of all the nitrogenized samples.

Dr. A. B. Wilder provided the oxygen determination in the Wemco iron sample.

Dr. H. H. Lester and Dr. L. R. Van Wert, of the Harvard faculty, maintained a constant interest and offered many helpful suggestions in these experiments.

Dr. B. A. Rogers assisted in the measurement of electrical conductivity.

DISCUSSION

(F. B. Foley presiding)

A. HAYES,* Middletown, Ohio.—There is one very interesting fact in connection with the data in this paper, which is that the carbon steel listed as sample A in Table 3, which contains 0.004 carbon, shows no quench aging, but I understand does show overstrain aging.

J. L. BURNS.—Dr. Hayes is correct in his assumption that the "pure" iron containing 0.004 per cent carbon shows age-hardening after plastic deformation, although it does not show age-hardening after rapid cooling. Since the former phenomenon (age-hardening after plastic deformation) has not been explained to the satisfaction of all, it is reasonable to take caution in differentiating the two.

F. B. FOLEY,† Philadelphia, Pa.—I wonder if I might ask Mr. Burns whether in aging the changes in properties were examined after very short periods of aging, of the order of minutes, following the quench?

J. L. BURNS.—The changes in properties were not studied after very short aging periods. Presumably Mr. Foley refers to the "incubation" period. In plotting "hardness" versus aging time in age-hardening systems there is a period immediately after quenching during which no hardening occurs. Consequently, this has been drawn in the systems reported as a horizontal line (parallel to the time axis). However, Dr. Jeffries has made a careful study of this period and cites his own results as well as the results of others, which indicate an actual softening of the material during this period.

MEMBER.—When nitrogen or carbon goes into solution in iron, where is it situated in the lattice itself? Is it interstitial or does it take the place of the iron in the annealed condition?

* Director, Research Laboratories, American Rolling Mill Co.

† Superintendent of Research, The Midvale Co., Nicetown.

J. L. BURNS.—The nitrogen atom, like the carbon atom, apparently locates in the interstices of the iron space lattice. This assumption is based upon the fact that the lattice parameter is increased by their introduction in solid solution. The nitrogen atom has a radius of 0.71 Ångstrom units and the carbon atom has a radius of 0.77 Å. Since the iron atom has a radius of approximately 1.24 Å, its replacement by a nitrogen atom or a carbon atom would require a decrease in lattice parameter. Therefore, the alpha iron-carbon and alpha iron-nitrogen systems must be interstitial solid solutions.

C. S. BARRETT,* Pittsburgh, Pa.—I would like to ask the author what precautions he took to prevent his X-ray results from being affected by internal stresses. This is important because a quenched steel almost always contains internal stresses, and such stresses are now known to alter the lattice dimensions as measured by X-rays. It is known, furthermore, that the distribution and intensity of quenching stresses are functions of carbon content. It seems possible, therefore, that the lattice dimensions given here may be altered by the carbon content by virtue of its effect on internal stresses rather than by solid solution distortion of the lattice, as Mr. Burns postulates.

The fact that the diffraction lines are sharp indicates only that there is no great inhomogeneity of stress in the samples, for it is the inhomogeneous (microscopic) stresses that widen the diffraction lines. If the samples contained stresses distributed uniformly over the surface (macroscopic, or homogeneous stresses) as the result of quenching from below A_1 —Buchholtz and his associates have found large stresses produced in this way in steel—the lines would be shifted rather than widened, and measurements of them would not give the true dimensions of the unstressed lattice.

J. L. BURNS.—Dr. Barrett has raised a very important point in his discussion of internal stresses, one that applies to the study of any such system as those reported.

The alloys considered in this paper cannot be called "quenched" steels in the ordinary sense. The quenching operation was performed while the alloys were in the alpha temperature range. Therefore no stresses would be set up such as might be incurred by the suppression of an allotropic transformation. The spectrum lines were always clear and sharp, so no microscopic stresses were present.

The precautions taken against the possible occurrence of internal stresses of a macroscopic nature was to use samples that had approximately the same dimensions in all directions and that were very small in volume.

Such stresses as those found by Buchholtz and his associates are not duplicated in these results. It will be noted that the "pure" iron did not show any change in lattice parameter. The addition of carbon through the range where it is soluble steadily increased the lattice parameter until a value of 0.035 per cent C. was reached. Increasing carbon above this value, even up to 0.85 per cent caused no further shifting of the spectrum lines. It should be noted that Buchholtz and his associates used bars and not small samples in their experiments. It is quite reasonable to expect macroscopic stresses from a shape such as they used. Furthermore, the change in lattice parameter is always associated with the disappearance of the precipitated phase on quenching from the temperature of maximum solubility. In the iron-nitrogen system, too, the lattice parameter continued to increase as nitrogen was introduced in solution.

F. B. FOLY.—The forms of curves of precipitation hardness plotted against time are typical and depend on temperature. At the optimum temperature for hardening by precipitation the hardness rises rapidly to a maximum and the maximum hardness is maintained for long periods of exposure at this temperature. When this optimum temperature is exceeded there is a more rapid rise to maximum hardness, but hardness then decreases more or less rapidly as the time of holding at temperature is increased.

* Metals Research Laboratory, Carnegie Institute of Technology.

At temperatures lower than the optimum temperature there is a gradual increase in hardness which persists for long periods of time, so that at low enough temperature many days are required to attain maximum hardness, if maximum hardness is attained at all.

A. SAUVEUR,* Cambridge, Mass. (written discussion).—Dr. Burns refers to the “knot” theory. Is it not in order to call attention to the purely speculative character of that theory? It was conceived to explain the behavior, or rather the misbehavior, of commercial duralumin on aging at room temperature. Something had to be done. It is permissible to carry the speculation further and to assume that the formation of knots within the solvent metal *always precedes* the precipitation of some of the solute. Admitting the formation of knots at room temperature, it is not readily seen why such knots should not be formed at a slightly higher temperature; namely, at 100° C. The fact that water boils at 100° C. while it does not boil at 20° C. suggests no explanation for the formation of knots at the lower temperature only. With this in mind, we would conclude that during the age-hardening of commercial duralumin at room temperature the first step of the phenomenon only takes place—namely, the formation of knots—resulting in increased hardness, decreased electrical conductivity and no change of parameter, whereas on aging at higher temperature the knot formation is so quickly *followed* by precipitation that the former cannot be observed and the alloy increases in hardness and in electrical conductivity while its parameter returns to the dimension of the parameter of the solvent. In instances where an increase in conductivity is observed not accompanied by a change in parameter, or when a change in parameter is accompanied by a decrease of conductivity, it might be inferred that the precipitation has proceeded sufficiently far to affect one only of the two factors. That this is speculation pure and simple is not denied. I should like to offer “knot” hardening as a better expression than “intrasolution” hardening to describe the hardening resulting from the formation of knots as distinguished from the hardening produced by precipitation, rightly termed “precipitation-hardening.”

J. L. BURNS.—Professor Sauveur brings out a very interesting point in his suggestion that knot formation is really the forerunner of true precipitation in all systems. In this he agrees with Professor Norton. It has been found to be true with systems where complete studies have been made.

A careful study over narrow temperature ranges in some systems might help considerably in systems that have not been shown to behave in this manner. However, even if this were not found to be true by such a study, the possibility could not be entirely eliminated. It may be that one process overlaps the other to such an extent as to make differentiation impossible.

Professor Sauveur's explanation of the behavior of the conductivity in various instances adds still more food for thought. These suggestions apparently depend upon the possibility that the X-ray diffraction apparatus is not sensitive enough to record precipitation in the small amounts necessary to bring about the differences in behavior noted. However, it is certainly no more speculative than the other explanations that have been offered.

J. T. NORTON,† Cambridge, Mass. (written discussion).—Dr. Burns has made a valuable contribution to the field of age-hardening, by showing that the low-temperature aging of these alloys of iron with carbon and nitrogen is not accompanied by precipitation. It is very interesting to find that the behavior of these interstitial solid solutions is similar to that of the substitutional type of solutions, of which duralumin is an example.

* Professor of Metallurgy, Harvard University.

† Associate Professor of Metallurgy, Massachusetts Institute of Technology.

The classification of age-hardening alloys has been made in this paper on the basis of two distinct hardening processes, one called "precipitation-hardening" and the other "intrasolution" hardening, and it is at least suggested that these two processes are more or less independent. It seems much more likely that both types of hardening are inherently present in all age-hardening alloys of this type (i.e., terminal solid solution type), and that the "intrasolution" process always precedes the precipitation process.

Very few systems have been studied with sufficient care to show whether or not this assumption is generally true, but there is some supporting evidence. In the case of duralumin, at intermediate aging temperatures, the hardness curve contains two distinct maxima, one occurring before precipitation takes place and the other corresponding to the precipitation. At lower temperatures the second peak never appears, and at higher temperatures the second peak spreads out to obscure the first. It seems clear that both processes are at work at all aging temperatures but that their relative influences on the property that we call hardness depend upon the temperature.

The writer has recently made some observations of the iron-rich iron-copper alloys that seem to confirm this idea. These alloys age-harden at temperatures above 300° C. and, in all cases, the aging is eventually accompanied by precipitation. The hardness curve, however, reaches a maximum at the point where the precipitation begins and the progress of precipitation is accompanied by a softening of the alloys. This is interpreted to mean that the "intrasolution" process is the important one in these alloys, and that the precipitation takes place either in the form of large crystals or crystals that rapidly agglomerate, so that precipitation actually detracts from the hardness rather than adds to it. In other words, the alloys begin to "overage" before precipitation is completed or perhaps even as soon as it begins.

It would be very instructive if the alloys used by Dr. Burns could be carefully studied at a series of higher aging temperatures. There is a very real need for more evidence of this sort on alloys of different types. It requires careful and painstaking work because usually the lattice changes are small, but the present paper shows that accurate and reproducible measurements are possible. The author of the paper is quite correct in emphasizing again the ambiguity of electrical measurements in studies of age-hardening.

J. L. BURNS.—Both Professor Norton and Professor Sauveur have suggested that knot formation may precede precipitation in all cases. Dr. Merica has suggested this possibility too. The difference in the behavior of the various properties during the aging of alloys necessitated a separation of the two processes. However, it was not intended that the two be taken as independent processes. As a matter of fact, the first alloy (duralumin) which showed the difference in behavior of these properties and which is one of the basic subjects of the paper would preclude such an assumption.

Professor Norton's statements on the iron-copper system are very interesting, especially that concerning the overaging that sets in immediately after the "intrasolution" type of hardening. This is another case where differentiating of the two processes will explain the changes in physical properties, but we should, as Professor Norton clearly indicates, remember that the two may not be truly independent.

X-ray Study of the Action of Aluminum during Nitride Hardening

BY JOHN T. NORTON,* CAMBRIDGE, MASS.

(New York Meeting, February, 1934)

IN spite of the very general employment of nitride hardening, there is still considerable doubt as to the real nature of the mechanism involved. Experience has shown that the addition of small amounts of hardening elements to iron or steel results in a wide variety of desirable properties in a nitrided case. Perhaps the foremost of these elements is aluminum and in this investigation an attempt has been made to study the behavior of aluminum during the hardening process. It is believed that the establishment of a complete atomic picture of the metal at various stages of the process will indicate the relationships between the several kinds of atoms and their individual influences on the physical properties in a clear and direct fashion.

A consideration of the problem suggests a surprising similarity between the mechanisms of nitride hardening and of age-hardening. It is now generally understood that age-hardening may take place by one of two distinct processes, the first involving the precipitation of a finely dispersed phase and the other being concerned with the modification of an existing phase. Following much the same line of reasoning, two theories of nitride hardening have been suggested. The first explanation, which has been generally discussed, particularly by Fry,¹ states in brief that the presence of aluminum causes the precipitation of aluminum nitride during nitriding and that this finely dispersed phase is the primary cause of hardening. The second explanation, which has not been published but which has been freely discussed by those interested in the problem, postulates the substitution of aluminum atoms for certain of the iron atoms in the several iron-nitrogen phases in the same manner that the substitutional iron-aluminum solid solution is formed. The marked increase in hardness, as compared with the aluminum-free system, is attributed to the severe lattice distortion accompanying this replacement.

Manuscript received at the office of the Institute Dec. 13, 1933.

* Associate Professor of Metallurgy, Massachusetts Institute of Technology.

¹ Fry: *Jnl. Iron and Steel Inst.* (1932) **125**, 191.

It should be possible to determine the correct explanation by experiment, and the most illuminating experiments are probably those that yield information about actual lattice changes. For this purpose, X-ray diffraction methods have been employed.

One may predict what lattice changes should be found experimentally as a consequence of these two theories. In the case of the aluminum-free alloys of iron and nitrogen, the structures have been carefully studied by

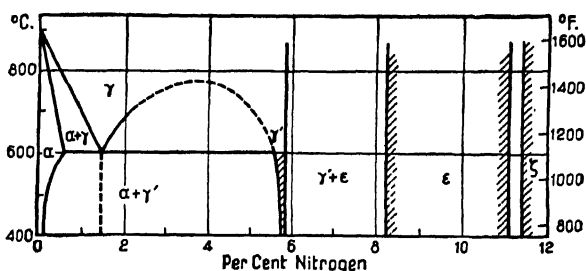


FIG. 1.—HÄGG'S IRON-NITROGEN DIAGRAM. (Reproduced from *National Metals Handbook*, 1933.)

Eisenhut and Kaup² and by Hägg³ and their results have been summarized by the author.⁴ Because of its agreement with the author's work, Hägg's diagram (Fig. 1) has been adopted in the present discussion. According to the substitutional theory, these same phases should occur in the aluminum-bearing alloys, but their parameters should be enlarged by an amount that is proportional to the amount of aluminum present. There is no reason to believe that the homogeneous ranges will be materially changed, but a definite increase in the broadness of the diffraction lines should appear to indicate the increasing lattice distortion.

If the precipitation theory is correct, one would expect to find a rather different picture. The first additions of nitrogen would go toward the precipitation of the aluminum as the compound AlN , and only after this has been completed and all aluminum removed from solid solution would the higher iron-nitrogen phases be formed. Thus the lattice constant of the original solid solution should drop sharply to the value for pure iron and then the iron-nitrogen phases could be formed entirely independently of the aluminum, so that their lattice parameters would be the same as found by previous investigators for nitrified pure iron. These phases would be homogeneous at higher total nitrogen contents by an amount corresponding to the quantity of nitrogen combined with alumi-

² Eisenhut and Kaup: *Ztsch. f. Electrochemie* (1930) **36**, 392.

³ G. Hägg: *Ztsch. f. phys. Chem.* (1930) **8**, 455.

⁴ J. T. Norton: *National Metals Handbook* (1933) 345.

num. The theory demands that aluminum and the iron form separate and independent phases with nitrogen.

EXPERIMENTAL RESULTS

The experience of the author and of others has shown that X-ray studies of the surface layers of nitrated samples are very unsatisfactory because of the broad diffraction lines obtained, due probably to a combination of effects. Measurements of the required accuracy are impossible from films showing such broad lines and, for this reason, powdered samples have been used for the present work.

Alloys of iron and aluminum were made by melting the desired quantities of electrolytic iron and aluminum of high purity in vacuum in a high-frequency induction furnace. The analyses of the iron and aluminum used are given in Table 1, also the compositions of the alloys as determined by analysis. Extraordinary purity is not necessary in an investigation of this sort.

The alloy ingots were reduced, by means of a fine file, to powder that would pass a 200-mesh sieve, and were nitrated in the powdered form. Experience showed that the structure was completely determined by the total nitrogen content if the samples were air-cooled from the nitrating temperature, so that the details of nitrating conditions have not been included. Each sample consisted of about one gram of powder and the nitrogen content was controlled by the nitrating temperature. The time of nitrating at each temperature was determined by experiment as sufficient to give as great a nitrogen content as possible. The rate of ammonia flow was kept constant by means of a flowmeter.

TABLE 1.—*Analysis of Metals and Alloys Used*

Electrolytic Iron Per Cent		Aluminum Per Cent	Alloys		
			Alloy	Weight Per Cent Al	Atomic Per Cent Al
C.....	0.00125	Si.....	A	0.00	0.00
Si.....	0.002	Cu.....	B	0.32	0.66
S.....	0.008	Fe.....	C	2.03	4.13
Mn.....	0.004		D	4.70	9.27
Al.....	0.004		E	10.14	18.9
P.....	0.002				

The X-ray examination of the powdered samples was carried out in the usual way, using focusing cameras of the type described by Westgren,⁵ and the radiation from a chromium target.

⁵ A. Westgren: *Trans. A. I. M. E.* (1931) **93**, Inst. of Metals Div., 14.

Two cameras were employed to cover the desired range of diffraction angles. In the case of films with very sharp lines, advantage could be taken of the added precision obtained at large diffraction angles. If the lines were slightly broadened, however, a high dispersion afforded no gain in precision and the intermediate camera had the advantage of shorter exposures. Since the precision of measurement of lattice param-

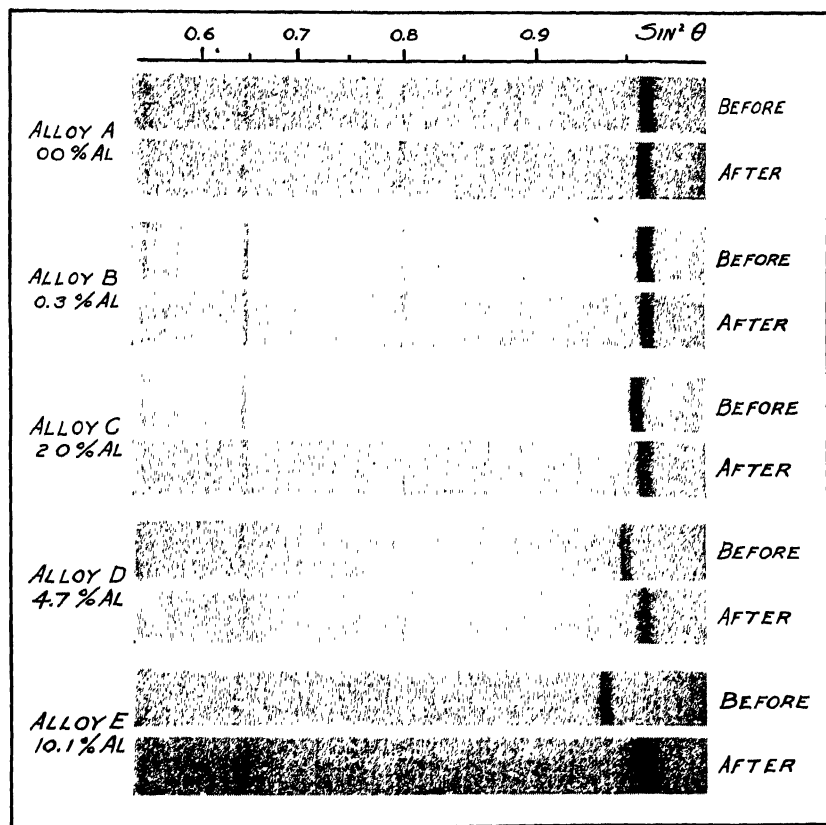


FIG. 2.—PHOTOGRAMS OF ALLOYS BEFORE AND AFTER NITRIDING, SHOWING ENLARGEMENT OF IRON LATTICE DUE TO INCREASING AMOUNTS OF ALUMINUM AND REMOVAL OF THIS ENLARGEMENT AS RESULT OF NITRIDING.

eters varies considerably in this work, the probable error is given for each value. This indicates the reproducibility of several photograms of the same sample.

The first series of experiments was for the purpose of studying the precipitation of aluminum nitride. A series of samples of varying aluminum content was nitrided at a high temperature (800° C. for 24 hr.), because this treatment produces only a very small amount of nitrogen in the iron phase. X-ray photograms were taken before and after nitriding

and a nitrogen determination was made of each sample. Fig. 2 shows the set of photograms obtained, while Table 2 gives the calculated values of the lattice constant, together with the original aluminum content and the final nitrogen content. In the last column of the table, the nitrogen content has been calculated on the basis that all of the aluminum is combined with nitrogen and that there is 0.015 per cent of nitrogen, the solubility limit at room temperature, in the iron phase.

The photograms show beyond question that all of the aluminum in each case has been precipitated, and the nitrogen analyses show that it must be in the form of the compound AlN . The slightly higher value of the observed nitrogen content is due to the fact that the solubility of the iron phase has been slightly exceeded and there is some of the next higher phase, Fe_4N , present. The very marked increase in the broadness of the lines of this photogram, as the amount of aluminum nitride increases, is evident.

The next series of experiments was made in order to show that lattice parameters of the various iron-nitrogen phases were independent of the aluminum content. For this purpose several series of iron-aluminum alloys were nitrided at a series of different temperatures so that a wide range of nitrogen contents was obtained. Table 3 gives the lattice con-

TABLE 2.—*The Alpha Phase*

Alloy	Weight Per Cent Al	Lattice Constants, Å.		Per Cent N	
		Before Nitriding	After Nitriding	Observed	Calculated
A	0.00	2.8606 ± 0.0002	2.8609 ± 0.0002	0.6	0.015
B	0.32	2.8613 ± 0.0002	2.8609 ± 0.0002	0.7	0.18
C	2.03	2.8664 ± 0.0002	2.8604 ± 0.0005	1.3	1.0
D	4.70	2.8749 ± 0.0002	2.8609 ± 0.0005	2.6	2.4
E	10.1	2.8911 ± 0.0002	2.861 ± 0.001	5.4	5.0

stants of the homogeneous gamma prime phase, which has a face-centered cubic structure. With the aluminum-bearing alloys, the lattice change within the narrow homogeneous range could not be detected because of a slight broadening of the lines, so that the figures given are really average values for this phase. Since the nitriding conditions could not be controlled to give exactly the homogeneous phase in each case, the nitrogen content was estimated from several films in the vicinity. In column 4 of Table 3 are found these estimated values, while column 5 gives the values calculated on the basis of 5.9 per cent of nitrogen in the iron phase (Fe_4N) and enough in the aluminum phase to form AlN with all of the aluminum present. The agreement is such that there can be no doubt of the independent nature of the iron and the aluminum phases.

The hexagonal epsilon phase in the aluminum-free system is homogeneous over a range from 8 up to 10 per cent nitrogen, and the lattice constants change markedly over this range. At the low nitrogen limit, the lattice parameter can be determined from samples lying in the two-phase field gamma prime plus epsilon. Table 4 shows that these parameters are independent of the aluminum content.

The upper limit of the epsilon phase in aluminum-free alloys is at about 10 per cent of nitrogen. This figure is somewhat lower than the 11 per cent set by Hägg, but a careful study, using pure iron obtained in various ways and with powders of varying size, shows conclusively that the limit lies between 9.9 and 10.2 per cent. The limit in aluminum-

TABLE 3.—*The Gamma Prime Phase*

Alloy	Weight Per Cent Al	Lattice Constants, Å.	Per Cent N	
			Observed	Calculated
A	0.00	$\{3.7894 \pm 0.0005\}$ $\{3.7913 \pm 0.0005\}$	5.9	5.9
B	0.32	3.789 ± 0.005	6.0	6.0
C	2.03	3.793 ± 0.005	6.8	6.7
D	4.70	3.794 ± 0.005	7.4	7.8
E	10.1	3.791 ± 0.005	9.0	9.8

TABLE 4.—*The Low-nitrogen Epsilon Phase*

Alloy	Weight Per Cent Al	Lattice Constants, Å.	
		a	c
A	0.00	2.692 ± 0.001	4.360 ± 0.002
B	0.32	2.70 ± 0.01	4.35 ± 0.01
C	2.03	2.69 ± 0.01	4.36 ± 0.01
D	4.70	2.70 ± 0.01	4.36 ± 0.01
E	10.1	2.70 ± 0.01	4.36 ± 0.01

bearing alloys is, of course, higher. In Table 5 are the parameters of a series of samples nitrided at a temperature that produces a nitrogen content close to this upper limit, together with nitrogen contents actually observed and those calculated on the basis of 10 per cent of nitrogen in the iron phase. The parameters agree closely but the observed nitrogen contents, although of the correct order of magnitude, are somewhat too low, particularly at the higher aluminum contents. This is believed to be due to a nonhomogeneous nitriding of the individual grains of powder, the analysis giving the average of each grain while the diffraction pattern comes only from the surface. One would expect this effect to be most

pronounced at the low nitriding temperatures necessary to produce the high nitrogen contents. It is also in line with observations in practical nitriding that have shown the very definite inhibiting action of aluminum on the diffusion of nitrogen. It is hoped that experiments with very much finer powders will settle this point.

In the case of the zeta phase, it has not been possible to obtain a high enough nitrogen content in samples containing more than one per cent of aluminum for this phase to appear. Apparently the presence of considerable quantities of aluminum nitride has so impeded the diffusion of nitrogen that an insufficient amount can be introduced at the low temperature to form this phase. It seems reasonable to assume that the non-appearance of this phase is an indication of the influence of aluminum on the diffusion of nitrogen rather than on the stability of the phase.

TABLE 5.—*The High-nitrogen Epsilon Phase*

Alloy	Weight Per Cent Al	Lattice Constants, Å.		Per Cent N	
		<i>a</i>	<i>c</i>	Observed	Calculated
A	0.00	2.754 ± 0.001	4.401 ± 0.002	9.9	10.0
B	0.32	2.75 ± 0.01	4.39 ± 0.01	9.8	10.1
C	2.03	2.76 ± 0.01	4.41 ± 0.01	9.8	10.7
D	4.70	2.75 ± 0.01	4.40 ± 0.01	10.4	11.5
E	10.1	2.75 ± 0.01	4.40 ± 0.01	12.2	13.3

Although the aluminum nitride is crystalline and its structure is known, no diffraction lines corresponding to this phase appear in any of the photograms. It can only be concluded that it is present in such a fine state of subdivision that it cannot be detected in this way. The indirect evidence of its presence, however, seems conclusive.

DISCUSSION OF RESULTS

An examination of the experimental results indicates a complete confirmation of the theory of precipitation as the principal cause of nitride hardening. The definite removal of aluminum from solid solution, and the fact that the lattice parameters of the iron-nitrogen phases are quite independent of their aluminum contents, are in complete agreement with the theory. The nitrogen contents of the various phases are also in general agreement. The only evidence not in complete agreement is the fact that at the higher aluminum contents and the lowest nitriding temperatures (about 400° C.) the nitrogen content of the alloys is slightly too low. The most logical explanation of this observation is that the diffusion of nitrogen, difficult enough at these low temperatures, is made more difficult by the presence of considerable aluminum nitride. Consequently, the nitrogen concentration in the iron phase of the aluminum-

bearing grains never reaches the same maximum value as in the aluminum-free grains. The distortion of the structure due to the presence of AlN, which is suggested by the broad diffraction lines, may also be a contributing factor in lowering the amount of nitrogen that the lattice is able to retain.

The precipitation theory, which these experiments seem to prove, receives considerable confirmation from practical nitriding experiments. Attempts to nitride at high temperatures, in order to obtain high penetration, followed by low temperatures to obtain high hardness, have been unsuccessful. The explanation of this is readily seen, for the high-temperature treatment has precipitated all of the aluminum nitride and has agglomerated the fine particles to a size too large to give maximum hardness. Further nitriding at a lower temperature only increases the nitrogen content of the iron phase, and this has little influence on the hardness. Several observers have shown that the maximum hardness of the nitrided case occurs in the alpha phase rather than at the outside surface where the nitrogen content is the highest. This indicates that the iron nitrides themselves are not the cause of hardness, but that the alpha phase is the most suitable as a matrix for hardening by the dispersion method. As far as the author is aware, there are no observations in the field of practical nitriding of the simple aluminum-bearing steels that are in opposition to the precipitation theory.

In view of the fact that two types of age-hardening are known to exist, one might ask whether the other type of nitride hardening should be expected under different circumstances. There is some basis for a prediction that the other type of hardening should be found under certain conditions. In the case of aluminum and magnesium, which form non-metallic nitrides, the precipitation-hardening should occur. On the other hand, if the hardening element is of the transition type, such as chromium, the nitrides are metallic and have the same interstitial structure as do the nitrides of iron, so that it is reasonable to suppose that the atoms of the hardening element would replace the iron atoms quite freely in the nitride phases. This hypothesis, which is, of course, pure speculation, could easily be tested and experiments are now under way for this purpose.

One might also ask why it is not possible to nitride an alloy of copper and aluminum and obtain a dispersion-hardening of the type described. The answer to this question is again based on the unique properties of the transition elements when combined with nitrogen. The ability of iron to form interstitial solid phases with nitrogen is the basic reason for the penetration of nitrogen and, without this penetration, the precipitation reaction cannot take place. Copper does not permit the penetration of nitrogen, for a reason which seems to be purely structural, therefore the hardness does not increase. By the same reasoning, a chromium-aluminum alloy should harden by precipitation. The ability of the

transition elements to form metallic interstitial compounds with nitrogen, as contrasted with the nonmetallic nitrides of certain other elements, is of fundamental importance to the problem of nitride hardening.

CONCLUSIONS

From the present experiments, it may be concluded that when ferrous alloys containing small amounts of aluminum are nitrided precipitation of aluminum in the form of the compound AlN takes place during nitriding, and that this phase distributed in a finely divided form throughout the iron matrix is the primary cause of hardness. The formation of the nitrides of iron is not influenced by the presence of aluminum and, while the possibility of their formation is of fundamental importance, their actual presence plays only a minor part in the hardening.

ACKNOWLEDGMENTS

The author wishes to express his indebtedness to Professor Arne Westgren and Dr. Gunnar Hägg, of the University of Stockholm, for their invaluable assistance during the early stages of this investigation.

He is also deeply grateful to his colleagues at the Massachusetts Institute of Technology for their many suggestions and kindly criticisms.

DISCUSSION

(Frank N. Speller presiding)

G. Hägg,* Stockholm, Sweden (written discussion).—The theory of precipitated aluminum nitride being a cause of hardness of nitrided aluminum-bearing steels was set forth by H. Hobrock and others, but it seems never to have been proved experimentally. Professor Norton's excellent work on this subject gives the first evidence of the existence of aluminum nitride and thereby opens a wide field for new research work on the nitriding of steels.

The fact that no lines of AlN can be detected even after a treatment at very high temperatures is somewhat astonishing, as one would expect a rather rapid crystal growth of the precipitated nitride at elevated temperatures. A possible cause may be that a growth is prevented by the iron matrix in which the small crystals are embedded. Anyhow, Professor Norton's determinations on the lattice dimensions seems to give sufficient evidence of the formation of an aluminum nitride.

Recent work on the Fe-Cr-N system carried out in this Institute by S. Eriksson indicates conditions analogous to the ones found by Professor Norton in the Fe-Al-N system. The chromium tends to take up as much nitrogen as possible under the formation of CrN , although the fact that chromium has less affinity to nitrogen than has aluminum makes the effect of chromium less pronounced than that of aluminum. In this case the formation of CrN can be shown directly in the photograms but the study of the phenomena is made more difficult by the existence of the hexagonal chromium nitride with approximate composition Cr_2N .

It therefore seems as if also transition elements could behave more or less in the same way as aluminum if their nitrogen affinity is high enough. In such cases, how-

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ever, the tendency of the transition elements to dissolve into the iron nitride phases might cause complications, as the nitrides of the alloying element might partly precipitate and partly form solid solutions with the iron nitride phases. In any case it seems unwise to say that transition elements cannot give rise to a hardening effect through nitride precipitation, although this effect may be expected to vary owing to the physical properties of the precipitated nitride.

Concerning the iron nitrides, Professor Norton says in his conclusions that "while the possibility of their formation is of fundamental importance, their actual presence plays only a minor part in the hardening." The relative sensitivity of the surface hardness of a nitrided steel to elevated temperatures seems however to be greater than could be expected if the hardness was due to AlN alone. The surface hardness of a nitrided steel drops rapidly when the temperatures (about 600° C.) are reached, where the decomposition velocity of the iron nitrides begins to obtain high values. On the other hand, it is not probable that the crystal growth of AlN has begun to any considerable degree of these temperatures. According to Professor Norton's experiments in Stockholm, the crystal growth of AlN is so slow—even at about 1100° C.—that no X-ray lines could be detected in preparations of nitrided aluminum steels heated for a week at this temperature. Further, it is a well-known fact that the mechanical properties of the nitrided surface are closely connected with its microstructures, which is to a great extent due to the iron nitride phases.

V. O. HOMERBERG,* Cambridge, Mass. (written discussion).—The author has rendered a valuable contribution to the subject of nitrogen hardening. In practical nitriding the maximum hardness is obtained after exposing the aluminum-bearing steel to ammonia gas at a temperature of about 500° C. A gradual decrease in the hardness is observed on nitriding at higher temperatures. Since Dr. Norton has shown that the hardness is produced as the result of the precipitation of the AlN particles, they must be of critical size at 500° C. His explanation for the lack of success in attempting to obtain maximum hardness together with increased depth by nitriding first at a high temperature (625° C.) followed by nitriding at a low temperature (525° C.) is entirely logical.

In determining the depth-hardness curves for nitrided steels, it is generally found that the maximum hardness occurs at a short distance below the surface, generally 0.001 to 0.002 in. J. W. Miller⁶ has shown that the nitrogen content drops very abruptly from the surface to this depth. In the case of the aluminum-chromium-molybdenum steel after nitriding at 525° C. for 48 hr., the nitrogen content dropped from about 10 per cent at the surface to 2 per cent at a depth of 0.002 in. The maximum hardness also occurred at this point where the lattice structure was found to be mainly body-centered.

The surface layer of the nitride case is generally brittle and is of the hexagonal close-packed type. Since it does not possess the maximum hardness, it is desirable to remove it by grinding to a depth of 0.001 to 0.002 in., thereby exposing a harder surface possessing less brittleness. Harder⁷ and Todd also found that the nitrided cases showing only the alpha iron lattice possess full hardness without objectionable brittleness. Obviously, it would be of great importance to the users of nitriding steels to be able to control the process so that only this phase would be produced. A change in steel composition might accomplish this goal.

* Associate Professor of Physical Metallurgy, Massachusetts Institute of Technology.

⁶ J. W. Miller: A Study of the Nitride Case in a Special Nitriding Steel. Master's Thesis, Massachusetts Institute of Technology, 1931.

⁷ O. E. Harder and G. B. Todd: Correlation of the Crystal Structures and Hardness of Nitrided Cases. *Trans. Amer. Soc. Steel Treat.* (1931) 19.

The author mentions aluminum and magnesium as two elements that form non-metallic nitrides and, for this reason, precipitation-hardening is to be expected. Undoubtedly boron and possibly titanium will behave in the same manner.

Since other elements, such as chromium, vanadium and molybdenum, are important for nitriding and, since they form metallic nitrides, it is hoped that the author will extend his research into a study of the mechanism of hardening when one or more of them are present.

After he has completed such an investigation, he will be able undoubtedly to explain the mechanism of nitrogen hardening of complex steels containing aluminum, together with elements such as chromium and molybdenum.

J. T. NORTON (written discussion).—It is very gratifying to find that those who have discussed this paper are in general agreement with the conclusion that there is a precipitation of aluminum nitride which accompanies the hardness increase during nitriding. The present experimental work has not given much direct evidence as to the actual mechanism of hardening in this case but has shown definitely that the precipitation must play a prominent role in any adequate picture of the process. The work also suggests a broad field of investigation of similar alloys and it is hoped that the collection of a considerable amount of data along these lines will be of assistance in the solution of the general problem.

Relation between Plastic Deformation in Deep Drawing and Tensile Properties of Various Metals

By M. H. SOMMER,* NEW YORK, N. Y.

(Detroit Meeting, October, 1933)

MANY attempts have been made to develop a relation between the tensile properties and the deep-stamping qualities of metals commonly used in deep drawing. These operations are generally performed cold and the metal is always stressed beyond the elastic limit. However, the problem cannot be readily solved without a proper investigation of: (1) the relation between actual stress and actual strain in the plastic range and (2) the stresses that are set up in the metal during the process of deep stamping.

Much work has been done in recent years to add to our knowledge on plastic deformation of metals and the shortcomings of the ordinary tensile test, particularly in the plastic range, have been sufficiently recognized. It has been widely acknowledged that the local contraction, which appears in a tensile test after the maximum load is reached, is not a general characteristic of the material but is peculiar to this form of testing. The plastic deformation of materials is explained by the slip of their crystals along certain planes and this rearrangement should be similar whether observed in a tensile, compression or torsion test, and if the results of any of these forms of testing show deviations, it must be due to other influences, as for example the local contraction in a tensile test. For this reason the tensile-test curve as obtained from the measurements taken on a tensile-test machine or registered by an autographic device has been supplemented by the so-called "actual stress-strain curve," which is constructed from the observed tensile-test data by eliminating the effect of local contraction and is in complete alignment with the stress-strain values obtained in a compression or torsion test. The actual stress-strain curve shows the increase of actual unit stress in relation to unit elongation beyond the yield point and beyond the point of maximum load and indicates clearly the extent of strain-hardening which the ordinary tensile-test curve does not reveal.

The following metals have been investigated in this paper and their actual stress-strain curves and, further, their deep-stamping char-

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* Consulting Metallurgical Engineer.

acteristics have been developed as shown in Table 1. The selection of these metals has been made with a view to comparing metals of well-known drawing properties with the stainless alloys for which sufficient information has not been collected as yet, so that a definite position among the other metals with regard to their deep-stamping qualities may be assigned to them. If their real drawing properties are once

TABLE 1.—*Data on Materials Investigated*

Material	Analysis	Ultimate Tensile Strength, Lb. per Sq. in.	Reduction of Area, Per Cent	Test Specimen	
				Length, In.	Diameter, In.
Armco ingot iron.	Regular	41,000	75	2	0.505
Copper.....	Pure	32,700	48	2	0.505
Brass.....	72.3 per cent Cu	39,800	30	2	0.505
Aluminum.....	98.6 per cent pure	14,200	30	2	0.505
Chrome steel A..	16 per cent Cr, 0.5 per cent Ni, 0.12 per cent C	79,800	66	3.2	0.800
Chrome steel B..	18 per cent Cr, 8.5 per cent Ni, 0.05 per cent C	105,700	73	2	0.505
Chrome steel C..	15.7 per cent Cr, 2.3 per cent Ni, 0.17 per cent C	128,600	57	3.2	0.800

established, the proper methods will be found in practice to process these alloys to the full extent of their possibilities. It must be stated here, with reference to the data on composition and mechanical properties in Table 1, that the selected materials have not been specially prepared to give the best deep-drawing characteristics that might be obtainable for any of these metals, but the vital factors for the deep-drawing qualities will be apparent from this investigation. If the mechanical properties are improved, the drawing qualities will be correspondingly enhanced; i. e., if the nominal ultimate strength can be raised without impairing the other properties the drawability will be increased.

ACTUAL STRESS-STRAIN CURVES

It is obvious that except for the reduction of area the usual tensile-test data do not represent the actual mechanical properties of the material, as the area of the cross-section of the test specimen decreases from the beginning of the test and the actual unit stress consequently is greater and steadily increasing as the test proceeds. This difference is small within the elastic range where the reduction of area is of limited proportions. In the plastic range the section area decreases rapidly, however, and the actual unit stress is increased accordingly. As soon as the contraction begins to be localized over a very small part of the test piece, the actual unit stress mounts rapidly to its greatest value at fracture. It must be observed here that such data on tensile tests can be used only

for the computation of the actual unit stress close to and at the breaking point, where the area of fracture has a geometrically perfect shape and the shearing of the ends is complete.

It has become customary to define the actual stress-strain curve as actual unit stress plotted against percentage reduction of area. In this form the curve represents the behavior correctly in the plastic range and many investigators have gone so far as to attach some definite importance to the intersection of this curve with the ordinate for the imaginary reduction of area of 100 per cent. However, such theoretical speculation has not yielded any useful information.

It seems more important for an analysis of various other forms of plastic deformation, as for example deep stamping, to base the actual stress-strain curve on the actual elongation. Up to the point of maximum load the elongation can be taken directly from the test measurements (known as uniform elongation). Beyond this point the elongation in a tensile test is localized at the point of local contraction and cannot be measured but may be computed from the measured reduction of area. The relation between reduction of area q and elongation Σ is expressed by the equation

$$\Sigma = \frac{q}{1 - q}$$

which has been developed under the assumption that the specific density of the material remains constant and the shape of the specimen keeps its cylindrical form.

The actual stress-strain diagrams in this paper (plotted on Fig. 4) were developed from figures averaged from several tensile tests of the material in a hydraulic tensile test machine. The tests were all taken on soft annealed hot-rolled bar specimens, the results on specimens cut lengthwise and across the grain were averaged and the ratio of gage length to test-bar diameter was kept constant in conformity with Barba's law of proportionality. The speeds of application of load were all within one and six minutes for the entire test and as the result is not appreciably affected within this speed limit no correction has been made for it. In general, every precaution was taken to arrive at values that represent the behavior of the material in the plastic range as truly as possible in the light of present-day knowledge. It is of no vital importance for this investigation, which only attempts to give the deep-stamping characteristics of a metal relative to other metals, whether these curves represent the "true" relation between stress and strain or not. No such claim could be made, and the curves, therefore, have been called "actual stress-strain curves" to avoid any misinterpretation.

These relations between the actual unit stress and the actual elongation form the base of this investigation and serve to find the stress that

must be applied to effect a certain plastic deformation of the material in deep drawing.

It is obvious that the physical properties of the material, such as homogeneity and structural characteristics, in the test piece should be as nearly alike as possible to the physical properties of the material in the form of sheets or strips in which it is subjected to the drawing operation. There will be some structural difference between the hot-rolled material and the hot or cold-rolled deep-drawing sheet in all materials, especially in the stainless alloys, and the actual conditions would be better represented by obtaining an actual stress-strain curve from a specimen of the sheet. The data of tensile tests on sheet specimens as they are taken today are not very suitable for the construction of the actual stress-strain curve because the results are in general too erratic, chiefly because the shape and the thinness of the test piece do not permit proper measurements of the reduction of area. These deficiencies could be overcome by a device designed to make simultaneous measurements of the change in width and thickness to obtain the instantaneous section area for instantaneous loads. The author suggests that some electrically controlled optical arrangement might be developed for this purpose. Actual stress-strain curves recently constructed from tensile tests on sheet specimens under the assumption that the ratio of width to thickness in the decrease of section area is maintained have shown a close conformity to such curves developed from tensile tests on hot-rolled bar specimens from the same material, and these results indicate that the deviations to be expected are actually not very great.

It should be remembered, however, in judging the final deep-stamping characteristics, that the refinement of the grain and other changes through subsequent work and heat treatment of the hot-rolled material will have a tendency to better the deep-stamping values that are based on the hot-rolled bar test.

ACTION AND REACTION IN DEEP DRAWING

Elsewhere¹ the author has analyzed the action and reaction in a deep-drawing operation in great detail. The plastic deformation that occurs when a flat disk is drawn into a shell by action of a punch is brought about by a number of composite stresses set up in different planes and different directions. These stresses are partly evolved by the forced rearrangement of the material and partly caused by the peculiar set-up which is required to accomplish this rearrangement. Consequently a study of the geometric relations between disk and shell and of the kinematic conditions of the operation must lead to a definition of these stresses.

¹ Versuche ueber das Ziehen von Hohlkoerpern. V. D. I. Verlag. Berlin, 1926.

There are three distinct forces which act upon the blank to deform it into the shape of the shell. By far the greatest of these is the composite stress, which compresses the portion of the flange that must be dislodged when the diameter of the blank is reduced to the diameter of the shell. This stress is set up around the entire flange in tangential planes. The resultant of all these tangential unit stresses may be called S .

The second of the three forces is the resistance caused by friction on both sides of the blank. The material being held tightly between two surfaces under a certain pressure, friction is created acting in a radially outward direction. This force measures a certain percentage of the normal blankholder pressure, its size being expressed by the product of normal pressure and the coefficient of friction. Assuming that the normal pressure does not change during the draw, as is the case in most double-action drawing presses, and that the lubrication is such that the coefficient of friction is also constant, the resulting friction does not change during the drawing operation. Naming the normal force or blankholder pressure H and the coefficient of friction μ , the resultant force is $2\mu H$.

The third and last of the three forces is evoked by the bending of the material around the drawing edge of the drawing die, a composite stress, which so far has steadfastly resisted all attempts to exact computation. The bending actually takes place in two planes because the material must be bent over the drawing edge, which in itself follows the curvature of the drawing die, in the case of a round shell a circle. All efforts to find a mathematical expression for bending materials beyond the elastic limit (*Ludwik*) have led to very complicated formulas, which furthermore apply to bending in one plane only. The experiments of the author have shown, however, that under conditions as they exist in deep stamping the bending of the material around the drawing edge sets up only a negligible stress in addition to the other stresses already acting upon the material. The experiments have been very conclusive on this point and the explanation for this result is quite simple and allows estimation of the error that will be made if the bending stresses are disregarded.

In bending material of a given thickness stresses are evoked over the entire cross-section, starting from the neutral axis (usually the center) towards the outer fibers in direct proportion to their distance from the neutral axis. The latter is not stressed at all provided that no other forces act upon the material, the extreme fibers on both sides showing the greatest stress, tension on the outside and compression on the inside. In deep drawing there is a large stress already set up, especially at the moment when the drawing power reaches its maximum. If now a bending stress is superimposed the additional lengthening of the extreme fiber on one and the corresponding compression of the extreme fiber on the other side requires only a very small increase in unit stress, as can be

observed from any actual stress-strain diagram. Most of the stress-strain curves flatten out in the upper regions and very little increase in unit stress will produce a wide change in elongation and compression. The stress-strain curves of some materials do not flatten out appreciably (brass, chrome steel B) and this fact should be considered in using the equations presented here, in which the bending stresses have not been taken into consideration.

There remains, therefore, the resultant compressive unit stress S and the friction $2\mu H$ which equate the drawing power P , the resultant of the tensile stresses set up in the wall of the shell by the punch of the press, leading to the fundamental equation for the deep stamping of a round shell (Fig. 1).

$$P = C^{\mu_1 \alpha} (2\mu H + 2\pi S) \quad [1]$$

C being the natural logarithm, α the angle of bending around the drawing edge (close to 90°) and μ_1 the mean coefficient of friction around the drawing edge.

The deep stamping of a round shell has been selected because it represents the most customary and simplest form of deep drawing, whereby

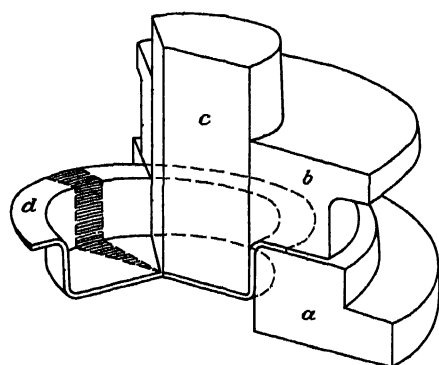


FIG. 1.—DIAGRAM OF DEEP STAMPING OF ROUND SHELL.

- a. Part of drawing die.
- b. Blankholder.
- c. Drawing punch.
- d. Partly drawn shell.

the stresses are symmetrically arranged around the circumference of the flange. In Fig. 1 a partially drawn shell is shown in such a way that the operation can be easily understood. a indicates part of the drawing die; b the blankholder, which rests on top of the blank under pressure to prevent wrinkling or buckling; c the drawing punch, which on its downward move draws the material into the die, and d the partly drawn shell. It is obvious that faulty construction of the drawing die, uneven, insufficient or excessive blankholder pressure, incor-

rect relation of the air space between punch and die to the thickness of the material and other details of design will cause additional stresses in the material, which must be avoided if full advantage is to be taken of the deep-stamping qualities of the metal.

The left side of equation 1 represents the external action brought by the punch and the right side the internal reaction set up in the material. The drawing power P is limited in its size by the nominal ultimate tensile

strength of the material; theoretically it can be equal but must in practice always be smaller than the ultimate tensile strength, allowing for a margin of safety for structural differences of the material, variations in thickness of the blanks, etc. If s represents the thickness of the material, πds the cross-section of the shell wall and σ_{\max} the nominal ultimate tensile strength, equation 1 takes the following form:

$$\pi ds \sigma_{\max} \geq C^{\mu, \alpha} (2\mu H + 2\pi S_{\max}) \quad [2]$$

This formula permits calculation of the first draw for any material, if its actual stress-strain curve, the blankholder pressure and the coefficients of friction are known. It is then necessary to add to the left side of equation 2 a safety factor, say 0.8 to 0.85, or when the material is very homogeneous, 0.9. The results will be fairly accurate if due consideration is given to the remarks that have been made about the bending stresses. To illustrate the satisfactory agreement of such a calculation with actual conditions, especially at the point where the drawing power reaches its maximum, two curves have been plotted in Fig. 2 showing the drawing power as function of the depth of the draw, one curve calculated from equation 2 and the other obtained from a drawing experiment on a test machine by an autographic device.

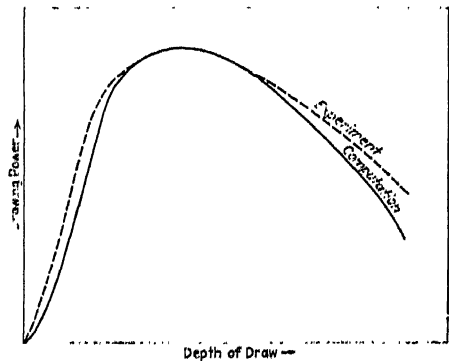


FIG. 2.—DRAWING POWER AS FUNCTION OF DEPTH OF DRAW.

The solid line shows a curve calculated from equation 2, the dotted line a curve obtained from an experiment on a test machine by an autographic device.

Equation 2 is given here solely as a fundamental formula for a comparison of the deep-stamping properties of various materials expressed in deep-stamping characteristics to be presently developed. This equation also forms the base for the considerations that finally led to the construction of the modified stress-strain curves that give a simple method of judging the deep-stamping qualities of any material by a transformation of its actual stress-strain diagram.

To develop comparative deep-stamping characteristics, equation 2 may be simplified by omitting the first term ($C^{\mu, \alpha} 2\mu H$), representing the ideal drawing process with the coefficient of friction zero; that is, without any friction at all. Such a state could be actually approached if the sliding friction under the blankholder could be replaced by rolling friction, as it appears for example in cold rolling. This omission of $C^{\mu, \alpha} 2\mu H$ is

justified here for two reasons. The error in fact does not exceed 10 per cent, which is the maximum value the friction will reach provided the material is properly lubricated to attain an appropriate coefficient of friction. For the object of comparing one material with another the error is much less, as the friction appears in both cases and its magnitude does not vary greatly for different materials as long as the nominal ultimate tensile strength of the materials compared does not show too great a difference. Equation 2 in this modified form reads then:

$$\pi d s r_{\max} \approx C^{\mu} \alpha 2 \pi S_{\max} \quad [3]$$

The coefficient of friction μ_1 around the drawing edge is also nearly alike for well lubricated surfaces of different materials and other conditions, as, material thickness and shell diameter being the same for two materials A and B , it follows:

$$\sigma_{\max}^A : \sigma_{\max}^B \approx S_{\max}^A : S_{\max}^B$$

This proportion means that two different materials will show the same deep-stamping qualities if their ratio of resultant compressive stresses to ultimate tensile strength is the same, and that these qualities of one material relative to another will be worse or better if its ratio is greater or less respectively, or: *all other factors being equal, the deep-stamping qualities of any material are in inverse proportion to the resultant compressive stresses divided by the nominal ultimate strength.*

DEEP-STAMPING CHARACTERISTICS

To develop the deep-stamping characteristics it remains to show the relation of the resultant S to the actual stress-strain curve and to compute S for various reductions in deep stamping independent of any specific blank or shell diameters.

S is the resultant of all the unit stresses acting in tangential planes which in turn are created by the amount of compression of every fiber in the flange. The extent of compression of every fiber Σ is determined by geometric principles and can be expressed for any radius x through the following equation for a round shell:

$$\Sigma = 1 - \frac{\sqrt{x^2 - 2r_1a_1 + a_1^2}}{x} \quad [4]$$

r_1 being the original radius of the blank and a_1 the distance the blank has moved towards the drawing edge.

Under the assumption that the stresses acting upon every unit in other planes and directions are relatively small and of little influence upon this deformation, the compression can be considered as created solely by the stresses acting in tangential planes, and the necessary unit stress to produce this deformation can be taken from the actual stress-

strain curve of the material. The sum of all these unit stresses σ over the entire area will then be the resultant S

$$S = \int \sigma df$$

or under consideration of the geometrical relations for the drawing of a round shell:

$$S = \int \sigma r S \frac{x}{\sqrt{x^2 - 2r_1 a_1 + a_1^2}} dx \quad [5]$$

For every position of the flange during the drawing operation the compression of every fiber Σ can be computed according to equation 4 and the unit stresses σ for this compression as represented by the actual stress-strain curve integrated over the entire area (equation 5) give the resultant S . It is obvious that the instantaneous values of S will be governed by the ratio of stress to strain expressed in the actual stress-strain curve and that the resultant S , therefore, is largely influenced by the shape of the actual stress-strain curve.

Equations 4 and 5 contain r_1 in several terms representing a specific blank diameter. For this investigation this dimension should be eliminated and a value substituted for S which has the same dimensions as the ultimate tensile strength, i. e., pounds per square inch, and is based on the reduction from blank to shell diameter in general rather than on specific blank diameters. This reduction may be designated w and using the following symbols that entered into equations 4 and 5 gives these formulas another form without changing their validity:

$$w = \frac{r_2}{r_1} \quad v = \frac{a_1}{r_1} \quad u = \frac{x}{r_1}$$

$$\Sigma = 1 - \frac{\sqrt{u^2 - 2v + v^2}}{\mu} \quad [4a]$$

$$S = sr_1 \int \sigma \frac{\mu}{\sqrt{u^2 - 2v + v^2}} du \quad [5a]$$

If the integral is designated I , its value will be proportional to S by the factor sr_1 . It is

$$I = \int_0^1 \sigma \frac{\mu}{\sqrt{u^2 - 2v + v^2}} du$$

The statements that have been made before with regard to S are, of course, applicable to I and the relative values of the deep-stamping qualities of any two materials can be measured by the ratio of the integral I to the nominal ultimate strength.

The integral I changes from zero (at the beginning of the draw) to a maximum and goes back to zero again (at the end of the draw). The

general type of the curves representing I (which is also the general type of the S curves) for various reductions w as function of the different

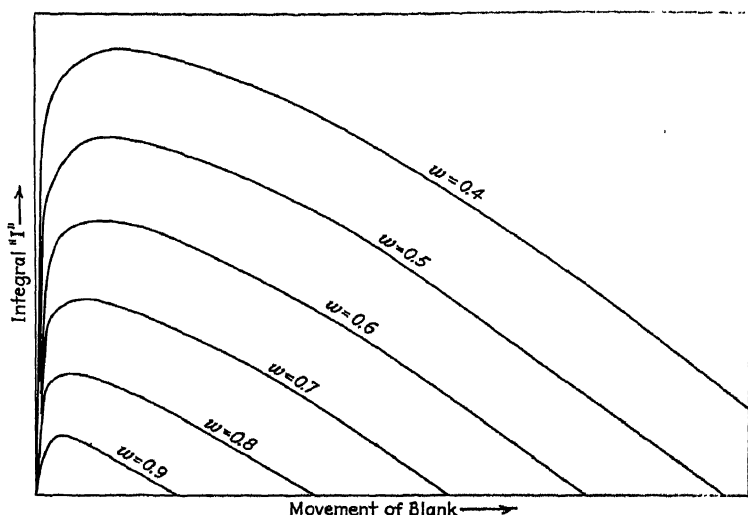


FIG. 3.—GENERAL FORM OF I CURVES FOR VARIOUS REDUCTIONS W .

positions of the outer edge of the flange during the draw is shown in Fig. 3. The maximum values of I are of sole interest for the determina-

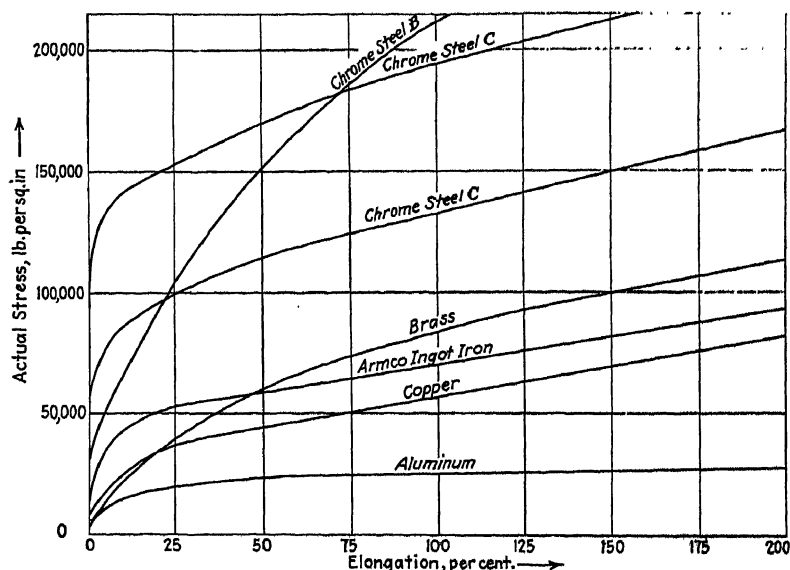


FIG. 4.—ACTUAL STRESS-STRAIN CURVES.

tion of the deep-stamping qualities and can be easily interpolated from the curves in Fig. 3. (An integration and mathematical determination

of the maximum for I is too difficult, as the actual stress-strain curve cannot be expressed in a simple equation).

If the deep-stamping quality may be designated as D then it is

$$D = \frac{\sigma_{\max}}{\vartheta_{\max}} \quad (\text{see page 280}) \quad [6]$$

The deep-stamping characteristics shall now be defined as the maximum reciprocal values of D plotted as function of various reductions w . The reciprocal values of D that represent the resistance to plastic deformation in deep stamping have been selected as indicators for the explicit reason of greater clearness in reproduction, which will also be apparent later on when the modified stress-strain curves are developed. The indicator for the deep stamping characteristics is then

$$\frac{1}{D} = \frac{\vartheta_{\max}}{\sigma_{\max}} \quad [7]$$

which shows the deep-stamping properties of the various metals sufficiently accurately for comparative purposes.

On Fig. 4 the actual stress-strain curves (stresses as function of unit elongation) of the materials investigated are shown and from these curves the integral I has been computed,² its maximum value for various reduc-

² The method for the graphical solution of the integral I has been fully set forth in the author's book on this subject (see footnote 1), where an example has been given for the computation of S from which the equation for I is derived. To find the maxima of the integral I as function of the reduction w , it suffices to select a few values of w , for example as shown on Fig. 3 ($w = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4$) and to compute and plot the values for I for each reduction w . For each such reduction various positions of the blank as designated by the movement of the outer edge of the blank are selected and the function under the integral is plotted for each position. For example, for a movement $a_1 = 0.2$ of the outer edge of the blank, each fiber will have moved a certain distance toward the center, and its deformation—within the limits of the integral and under consideration of the reservations made on page 280, last paragraph—may be found from equation 4a. The actual stress-strain curves then furnish the stress in each fiber corresponding to the deformation found. To plot the curve representing the function under the integral I a sufficient number of fibers are selected, their strain computed, their stress taken from the actual stress-strain diagram and the resulting values plotted on cross-section paper. The curve drawn through the points plotted represents the function under the integral for the position of the blank at $a_1 = 0.2$, and the area between the abscissa and the curve within the limits of the integral (see equation 5a) gives the value of the integral for this position of the blank. The integrals for other positions a_1 of the blank are similarly found and show if plotted as function of a_1 the form as reproduced on Fig. 3. As can be seen from the character of these I curves on Fig. 3, there is one position a_1 of the blank for every reduction where the integral I reaches a maximum; i. e., the material is under its greatest stress. If the material stands this maximum stress it will satisfactorily pass through the reduction, which means that only the maxima of I are of interest and these values can be easily interpolated (see Fig. 3).

tions interpolated and plotted as function of these reductions. In dividing the ordinates by the nominal ultimate strength according to equation 7 the deep-stamping characteristics were found and reproduced in Fig. 5. The lowest values on Fig. 5 represent the best drawing qualities for each reduction as the reciprocal values of the deep-stamping quality have been plotted.

The curves refer only to fully annealed material which has not been subjected to any stress previous to the drawing operation.

Fig. 5 shows that the deep-stamping properties are best for brass (72.3 Cu) up to a reduction of 0.575. Next follows the 18 per cent Cr,

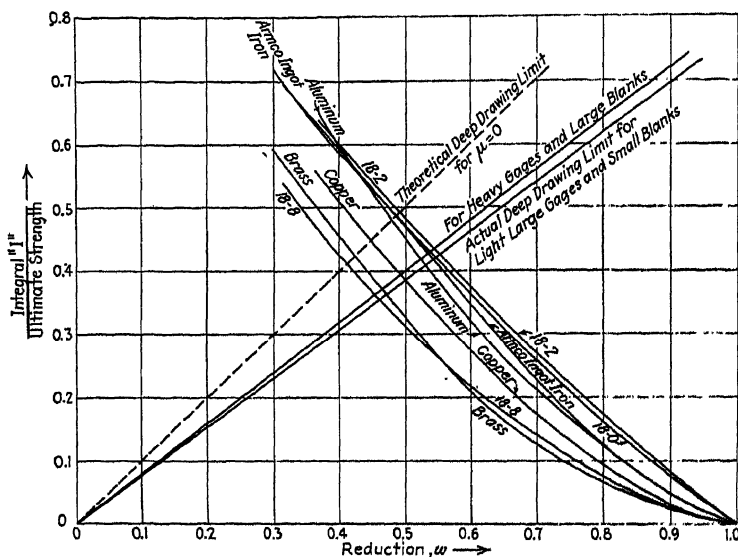


FIG. 5.—DEEP-STAMPING CHARACTERISTICS.

8 per cent Ni stainless alloy, which gains this position by its extraordinarily high tensile strength (105,700 lb. per sq. in., a figure that represents the latest accomplishment in raising the tensile strength of this composition through alloying additions without losing ductility). Then comes copper and aluminum, followed by Armco ingot iron, and finally the two other stainless alloys, the 18 per cent Cr, and the 18 per cent Cr, 2 per cent Ni composition. To ascertain the best drawing composition of any alloy it is an easy matter to plot, for example, different kinds of brasses and find the best drawing composition or check any other constituents of metals and their heat treatments. These deep-stamping characteristics give information on the deep-stamping qualities of metals in the same way that the tensile test curves furnish data on the mechanical properties of materials.

Many conclusions might be drawn from these curves that might prove helpful in many directions. To mention only one observation, it appears that any variation in nominal ultimate strength that might be accomplished through the addition of alloying elements without greatly changing the general character of the actual stress-strain curve will produce a wide change in the relative position of the deep-stamping characteristic of the basic material. In this connection the 18-8 chrome-nickel steel and aluminum might be mentioned.

The formula from which the deep-stamping characteristics were deduced have been confirmed by empirical tests and there seem to be no other data in the literature by which the accuracy of these curves could be checked. The deep-drawing properties as measured by the Erichsen cup test are reproduced for various materials in Fig. 6. The drawing qualities of the different metals shown have the same relative position to each other as the curves in Fig. 5, the latter inversely, of course. Besides, the Erichsen values are apparently given for the best deep-drawing qualities available of each metal.

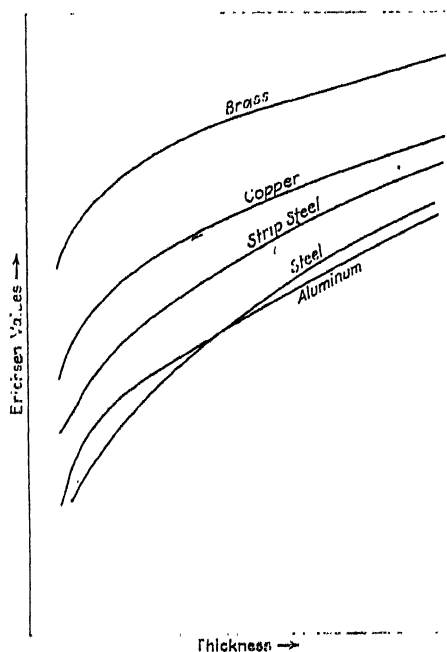


FIG. 6. ERICHSEN VALUES.

MODIFIED STRESS-STRAIN CURVES

It appeared to the author during this work of computing the deep-stamping characteristics, which, in spite of all the simplifying assumptions made is still quite complicated, that a much simpler and quicker determination of the deep-stamping qualities of metals might be possible by substituting for the integral I the ordinates of the actual stress-strain curve themselves and to find an indicator for the deep-stamping characteristics in dividing the ordinates of the actual stress-strain curve by the nominal ultimate tensile strength.

This would, indeed, be a surprisingly simple way to obtain information on the drawing qualities of materials. The author has considered the possibility of such a substitution from all angles and has finally come to the conclusion that the ratio of unit stress to ultimate tensile strength can actually be accepted, with certain reservations and if interpreted

with proper precaution, as an indication of the relative position of metals with respect to their drawing qualities. This transformation of the actual stress-strain diagram and its significance can be worded as follows:

All other factors being equal, the deep-stamping qualities of any material are in inverse proportion to the position of its modified stress-strain curve found in dividing the ordinates of its actual stress-strain curve by the nominal ultimate tensile strength.

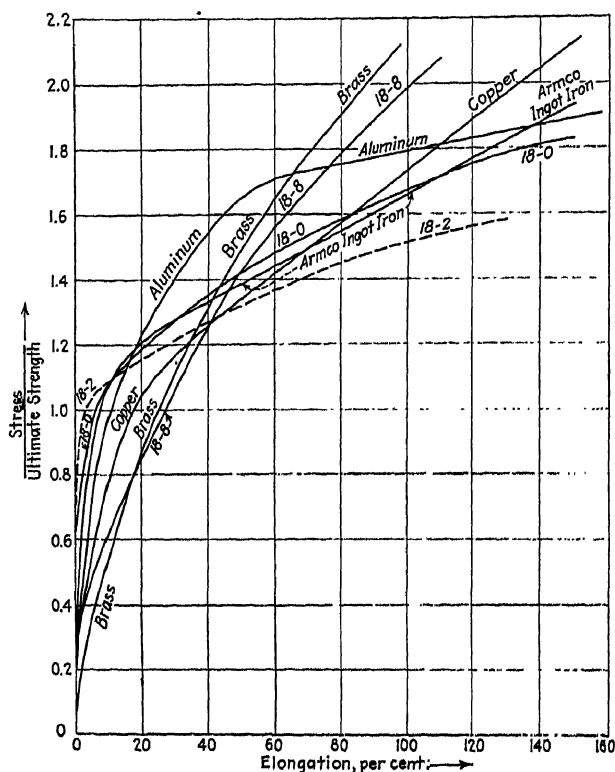


FIG. 7.—MODIFIED STRESS-STRAIN CURVES.

In compliance with this statement, the actual stress-strain curves of Fig. 4 have been so transformed and the resulting values have been plotted in Fig. 7. The author has called these curves "modified stress-strain curves," because they represent the conditions of actual stress and strain obtained from a tensile test so modified that they indicate the drawing qualities of the material over the entire range of plastic deformation.

It must be understood that the modified stress-strain curves do not furnish any absolute values of the extent of plastic deformation in deep drawing. Like the deep-stamping characteristics, they only show whether a certain material will draw or should draw better or not as

well as some other material. If the drawing qualities of one material are well known an indication of the deep-stamping possibilities of some other material might be found in the relative position of its modified stress-strain curve. Such a quick determination should be of considerable assistance in developing new deep-drawing compositions and in checking the actual performance in deep stamping with the possibilities indicated by this curve. It is a well-known fact that the excellent drawing qualities (for the annealed material) of the 18 per cent Cr, 8 per cent Ni stainless alloy have not been recognized in practice for some time because of radical changes that were necessary in the design of drawing die and press. As long as the proper practice had not been developed failures were charged to the low drawability of the alloy. Warning must be given of the possible danger in accepting the modified stress-strain curves in lieu of the deep-stamping characteristics. All the assumptions that have been made for the development of the latter have been tested by experiments and have been found to be permissible, while the substitution of the actual unit stress for the integral I (or in a wider sense for the resultant S of all the compressive stresses) is a simplification that is open to much criticism, in spite of the fact that it suggests itself so readily and that it gives apparently satisfactory results.

It must be remembered, in judging the deep-stamping quality from modified stress-strain curves, that two important assumptions have been made, for which proper allowance should be given where necessary. The bending stresses have been disregarded as negligible, but they will influence the final results if the actual stress-strain curve of the material does not flatten out perceptibly in the plastic range, and any additional stresses set up for bending the metal around the drawing edge will lessen the drawability of the material.

The friction stresses have been considered in the fundamental equation 1 for the drawing process but have later been omitted under the assumption that they will be approximately the same for different materials. This will not hold true for materials with widely different ultimate tensile-strength values and surface conditions. High ultimate strength necessitates a greater blankholder pressure and in turn produces greater friction even if the coefficient of friction could be kept the same as for materials of lower tensile strength through proper selection of the lubricant. Certain materials, furthermore, are what is called "self-lubricating," while others show a tendency in the opposite direction. If the friction is greater for one material, its drawing values will also be lower.

Another point, which has not been considered as yet, is the speed of the drawing operation, which is greatly in excess of the speed in any testing machine. In so far as different materials show similar changes in mechanical properties if a higher rate of speed is applied there will be

no influence but any probable greater difference in any of the properties by some material should be given due consideration.

In spite of these reservations, which must be made in interpreting these curves, their simplicity is striking and the relative position of the curves in Fig. 7 corresponds closely to the deep-stamping characteristics and Erichsen values, and is in satisfactory agreement with the practical experience on the drawing properties of these metals. Furthermore, the modified stress-strain curves give information on the probable behavior of metals in deep drawing *to the full extent* of their plastic deformation.

All investigations on the deep-stamping properties of metals have been limited heretofore to an analysis of the drawing of the annealed material in a so-called "first" draw³ and no predictions on the drawing qualities of metals already strain-hardened could be made except from observations obtained in empirical tests and in practice.

The material that has passed through the first drawing operation is strain-hardened, and if not annealed it requires greater stresses for further cold deformation in redrawing. This behavior might be explained as a composite stress composed of a stress required in accordance with the deformation that has already taken place and an additional stress to produce whatever further deformation is called for in the subsequent draw (provided the computation is based on the actual stress-strain curve of the annealed material).

Certain conclusions on the probable behavior of the investigated materials in redrawing can now be drawn from the modified stress-strain curves in examining the higher regions of plastic deformation. As Fig. 7 shows, the various curves change their relative position if the plastic deformation is extended.

The 18 per cent Cr, 2 per cent Ni composition assumes a unique position in reversing entirely its original relative drawability. The form of the curve for the 18-2 alloy seems to indicate that this alloy can be redrawn with ease and might not require annealing to effect substantial plastic deformation in drawing. Considering the high tensile strength of the 18-2 stainless alloy, an allowance for increased friction must most certainly be made, however, and this might lower the indicated drawing properties for redrawing to some extent. The author has just started a series of practical tests on the 18-2 composition, as very little information could be found in the literature to check whether the actual drawing qualities of the alloy conform with the properties indicated by its modified stress-strain curve. The results of these experiments will be published in due course.

Next to the 18-2 stainless variety, the other metals assume relative positions that correspond fairly well to their actual performance known

³ The author is now working on a mathematical formulation of the conditions in subsequent drawing operations of strain-hardened material.

in practice. Copper gains quickly the best deep-stamping qualities and the general character of its modified stress-strain curve relative to the other curves suggests uniform properties, which together with its low ultimate strength and self-lubricating qualities gives this material the position it holds among the deep-drawing metals. For extremely heavy cold deformations copper is susceptible, however, to somewhat greater work-hardening than some of the other materials.

Armco ingot iron, representing a typical low-carbon steel for deep drawing, and the straight 18 per cent Cr stainless iron, which behaves very much like Armco ingot iron, also improve their drawing properties with increasing plastic deformation and show little work-hardening.

Brass of a composition selected here (72.3 per cent Cu) and the 18-8 chrome-nickel steel lose considerably on drawability in extended deformation, showing extreme work-hardening and soon reaching a stage where the possible reductions in subsequent draws would apparently become so small that it would not be economical to further process them without annealing. The behavior of these two alloys is well known and it is gratifying to see how well their modified stress-strain curves correspond with actual experience.

Aluminum also assumes a peculiar position in Fig. 7, as it betters its place with the extent of its deformation. There is considerable strain-hardening at the early stage of plastic deformation but once beyond this range the modified curve for aluminum flattens out perceptibly, indicating that even after large plastic cold deformation satisfactory reductions should be possible without fracture of the material, a performance that is also well confirmed by the actual behavior of the deep-drawing grades of aluminum.

Summing up, it can be stated that the divergencies of the modified stress-strain curves of the various metals investigated correspond closely to their known behavior in deep drawing and that all the deductions made follow readily from the character of these curves and do not require the usual twisted and doubtful explanations necessary when a questionable theory is brought into alignment with actual performance.

LIMIT FOR FIRST DRAW ACCORDING TO DEEP-STAMPING CHARACTERISTIC

To estimate the extent to which a metal can be deformed in the first draw without fracture, equation 2 may be used by substituting for S the integral I as follows:

$$\pi d s_{\max} \cong C^{\mu_1 \alpha} (2\mu H + 2\pi s r_1 \vartheta_{\max}) \quad 2a)$$

This equation can be written in the following form:

$$\frac{\vartheta_{\max}}{\sigma_{\max}} \cong \frac{w}{C^{\mu_1 \alpha}} - \mu \frac{H}{\pi \sigma_{\max} s r_1} \left(w = \frac{r_2}{r_1} \right) \quad [8]$$

which has on its left side the values of the ordinates in the diagram of the deep-stamping characteristics (Fig. 5).

For the ideal state without friction the coefficient of friction is zero and equation 8 takes the following form:

$$\frac{\vartheta_{\max}}{\sigma_{\max}} \approx w \quad [9]$$

The line representing this formula has been drawn into Fig. 5 (dotted line) showing in the intersection of this line with the deep-stamping characteristics the limit to which the material could be drawn provided there were no friction and, of course, no margin of safety.

To make proper allowance for the friction, equation 8 must be considered. The first term on the right side must be divided by $C^{\mu, \alpha}$ and assuming a mean value for the coefficient of friction $\mu = 0.15$ and the angle of the drawing edge $\alpha = \pi/2$, as mostly in practice, the value for $C^{\mu, \alpha}$ is 1.265. The second term of equation 8 is very small and diminishes with increasing blank diameters and thickness of the blank very rapidly.

To represent these conditions, two additional lines (solid lines) have been drawn on Fig. 5. One line shows the actual deep-drawing limit for heavy-gage material and large blanks, and the other line the limit for light gages and small blanks. As before, their intersection with the deep-stamping characteristics indicates the limit to which the material can be reduced without fracture. This limit will be further reduced in practice, as a safety factor must be allowed.

It must again be emphasized that the indicated drawing limits as well as the deep-stamping characteristics have no absolute meaning and should be judged only under due consideration of the various reservations, which have been referred to on numerous occasions in this paper. If used in such a way these curves should be of value and should facilitate the explanation of many failures and prove its worth in further research on the deep-drawing properties of metals and on the probable behavior of new alloys or alloying additions to basic materials.

There is one problem in deep drawing which has not been discussed in this paper because it does not find a direct explanation through the deep-stamping characteristics or the modified stress-strain curves. This is the appearance of surface strains on deep-drawn shells, often called orange peel, and their probable relation to the flow figures or Lüder's lines observed on tensile-test specimens of certain materials.

SUMMARY

It has been shown that an intimate relation exists between the actual stress-strain curve with the actual elongation as abscissa and the deep-stamping properties of metals.

The equations that represent the conditions of stress upon the material in a deep-drawing operation have been briefly explained and the extent

of their agreement with the actual deformation in deep drawing has been outlined. Based on these equations, deep-stamping characteristics have been developed for various metals, showing the relative deep-drawing properties of these materials and leading to the following statements:

1. All other factors being equal, the deep-stamping qualities of any material are in inverse proportion to the resultant compressive stresses divided by the nominal ultimate strength.

2. All other factors being equal, the deep-stamping qualities of any material are in inverse proportion to the position of its modified stress-strain curve found in dividing all unit stresses by the nominal ultimate strength.

The curves that have been constructed in accordance with these statements are in satisfactory agreement with experiments and actual practice, in particular with the Ericksen values on deep-drawing properties.

The modified stress-strain curves lead to valuable conclusions on the behavior of the metal in subsequent drawing operations without intermediate annealing and show clearly the effects of the work-hardening of certain metals in such operations.

The limits to which the metal can be drawn in a first drawing operation without fracture have also been shown under the assumption of the ideal state of drawing without friction and under conditions closely approaching the actual performance in practice. Straight lines expressing these limits have been entered into the diagram of the deep-stamping characteristics, also conforming satisfactorily with actual experience. They are in agreement with the known fact that the permissible reduction in one draw is less for thin-gage material and small blank diameters than for metal of heavier gage and large blank diameters.

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